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Bioavailability of N, P, K, Ca, Mg, S, Si, and Micronutrients

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11.1 Bioavailability of Nitrogen

James J. Camberato

11.1.1 Introduction

The focus of this chapter is to illustrate how the fundamental transformations and transport of nitrogen (N) in the soil alter its bioavailability and impact plant productivity and environmental quality. Nutrient bioavailability or availability can be defined in many ways. Of the 10 definitions described by Blackmer (1999), that of Peck and Soltanpour (1990, p. 4) is most appropriate to this chapter: "By plant-available nutrient, one usually means the chemical form or forms of an essential plant nutrient in the soil whose variation in amount is reflected in variations in plant growth and yield."

The transient nature of N in soil and the large quantity accumulated by plants both contribute to the frequent occurrence of N deficiency in nonlegumes. Maximizing N bioavailability from indigenous soil N and added N (fertilizer, manure, legume residues, etc.) to optimize the yield of crop plants was the initial impetus to understanding N bioavailability. Considerable study of N transformations and transport determined that the processes of mineralization and immobilization, nitrification and denitrification, volatilization, and leaching control N bioavailability. With time, it was realized that N losses from agricultural systems via leaching, denitrification, and ammonia (NH_3) volatilization impacted surface and ground water, atmosphere, and noncultivated ecosystems; and much emphasis was then placed on quantifying and understanding these effects as well.

11.1.2 Nitrogen Cycle

Nitrogen bioavailability to plants is dynamic—the result of several interrelated microbial, chemical, and physical processes in

soils, which are contingent upon the nature of the soil as well as temperature, moisture, energy, and other factors. The connectivity of these processes is often displayed as "The Nitrogen Cycle" (Section 27.1 of *Handbook of Soil Sciences: Properties and Processes*).

Nitrogen inputs to soils include N fixation, atmospheric deposition, and purposeful nutrient application (fertilizers, manures, etc.). Although dinitrogen gas (N_2) comprises ≈80% of the atmosphere, it can only be utilized by a few species of free-living bacteria and blue–green algae, and specialized N-fixing bacteria that form symbiotic relationships with leguminous plants (Section 27.1 of *Handbook of Soil Sciences: Properties and Processes*). Historically, the majority of reactive N (N molecules other than N_2) arose from microbial N fixation, until the recent (geologically speaking) development of the Haber–Bosch fertilizer manufacturing process (Galloway and Cowling, 2002; Mosier, 2002). The only other natural processes contributing significantly to the oxidative fixation of N_2 are lightning (Noxon, 1976; Liaw et al., 1990), fire, and volcanic activity (Bandy et al., 1982; Huebert et al., 1999).

With the industrial revolution came an increase in atmospheric deposition of reactive N, mostly due to the burning of N-containing substances. More than 90% of the N in organic residues is lost to the atmosphere with burning (Heard et al., 2006), most as NO_x (nitric oxide [NO] and nitrogen dioxide [NO_2]), nitrous oxide (N_2O), NH_3, hydrogen cyanide (HCN), and higher N-compounds (Lobert et al., 1990). On a global scale, atmospheric N deposition from anthropogenic sources has exceeded that from natural sources since the mid-twentieth century (Galloway, 2001) and was recently estimated to be about fourfold that from natural sources (Fowler et al., 2004). Smil (1999) reported wet deposition of 1 kg N ha^{-1} in the United States, west of the Mississippi, 7 kg N ha^{-1} in the coastal Northeast, and as much as 20 kg N ha^{-1} in the Netherlands, northeastern France, and southern England. Although the deposition of reactive N might be viewed positively in its contribution to plant productivity, atmospheric N deposition also contributes to soil and water acidification (Galloway, 2001; Rodhe et al., 2002), eutrophication of surface waters (Fisher and Oppenheimer, 1991; Bergström and Jansson, 2006), and decreased ecosystem diversity (Bobbink et al., 1998; Lee and Caporn, 1998). Additional beneficial and detrimental effects of reactive N in the environment are overviewed in Section 27.5 of *Handbook of Soil Sciences: Properties and Processes* and Galloway and Cowling (2002).

11.1.3 Nitrogen an Essential Plant Nutrient

"Nitrogen is without doubt the most spectacular of all essential nutrients in its effect on plant growth" (Olson and Kurtz, 1982, p. 568). Plant growth responses to increasing N bioavailability are more frequent and larger than to any other essential nutrient. Viets eloquently stated, "No one can claim that N is more essential than any of the other 15 elements known to be needed for higher plants, but on the basis of relative number of atoms needed, N is at the top of the list of those that come from soil or fertilizers," (Viets, 1965, pp. 503–504). Nitrogen is a component of nucleic acids (RNA and DNA), amino acids (proteins and enzymes), and chlorophyll. Detailed information on the role of N in plant nutrition can be obtained from Lea and Morot-Gaudry (2001) and Amâncio and Stulen (2004).

Plant tissue sufficiency concentrations of N differ among plant species and plant parts, ranging from ≈20 to 50 g N kg^{-1} as reported by Olson and Kurtz (1982). Legumes have higher tissue N concentration than nonlegumes, >40 versus <40 g kg^{-1}. Most plant N is in the organic or reduced form, although nitrate (NO_3^-) will accumulate to some extent in some situations (Grunes and Allaway, 1985, pp. 594–597). Aboveground N accumulation may exceed several hundred kilograms per hectare in productive environments, but in most environments N bioavailability limits the growth of nonleguminous plants.

Inadequate N bioavailability reduces overall plant growth and often results in chlorosis (yellowing) of plant tissues, a result of reduced chlorophyll content. Since N is highly mobile in the plant, chlorosis and necrosis of older plant tissues precedes the chlorosis of younger tissues, as N is translocated from older to younger plant parts. Descriptions and photographs of N deficiency on many important grain, sugar, oilseed, vegetable, and fruit crops as well as turfgrasses can be obtained from Bennett (1993). Excess N can also have detrimental effects on plants; including delayed flowering, reduced fruit set, and increased lodging. Excess N can impair the utilization and quality of crop plants, including poor wear tolerance of turfgrasses, reduced sugar concentration of sugar beets, lower tobacco leaf quality, and excessive NO_3^- content of vegetables and forages.

11.1.3.1 Nitrogen Uptake by Plants and Microorganisms

Nitrogen is accumulated by plants from the soil as the anion NO_3^- and the cation NH_4^+. Most plants readily accumulate both inorganic forms, with perhaps the exception of blueberry (*Vaccinium corymbosum* L.; Claussen and Lenz, 1999) and cranberry (*V. macrocarpon* Ait.; Greidanus et al., 1972), which often demonstrate a strong preference for NH_4^+. Some nondomesticated plants may have a preference for NH_4^+ or NO_3^-, depending on their adaptation to soil pH and the predominant form of N naturally occurring in the soil. Species adapted to acid soil environments may prefer NH_4^+ (Atkinson, 1985); the most prevalent form of N in acid soil, whereas less acid-tolerant species may prefer NO_3^- (Gigon and Rorison, 1972). However, many nondomesticated plants, as do crop plants, grow best on a mixture of NH_4^+ and NO_3^- (Rorison, 1985; Falkengren-Grerup, 1995). Nitrogen accumulation by plants can be rapid. Bowman et al. (1989) calculated a rate of ≈35 kg N ha^{-1} day^{-1} for field-grown, moderately N-deficient Kentucky bluegrass (*Poa pratensis* L.). In Maize (*Zea mays* L.), N accumulation rates peaked between 5 and 15 kg N ha^{-1} day^{-1} (Karlen et al., 1987).

Heterotrophic microorganisms accumulate NH_4^+ over NO_3^- when both are present (Jansson et al., 1955; Wickramasinghe

et al., 1985; Rice and Tiedje, 1989), but will readily accumulate NO_3^- if it is the only form present (Davidson et al., 1990; Recous et al., 1990). Microorganisms are more competitive for N than plants in the short term. In 24 h ^{15}N uptake studies conducted in a Mollic Haploxeralf, annual grassland plants accumulated NO_3^- and NH_4^+ at rates of 0.6 and 1.0 kg N ha^{-1} day^{-1}, respectively (average for April and February measures), whereas microbial uptake was two- to fivefold higher at 1.1 and 5.3 kg N ha^{-1} day^{-1} (Jackson et al., 1989).

11.1.3.2 Ammonium and Nitrate Nutritional Effects on Plant Growth and Development

Many greenhouse, growth chamber, and hydroponics experiments demonstrated greater N uptake and/or growth of several crop species when provided both NO_3^- and NH_4^+, compared to a preponderance of one N form over the other (Schrader et al., 1972). Since NO_3^- is the predominant form of N available to plants in most cultivated soils, a nitrification inhibitor is often used to increase the proportion of total N that is in the NH_4^+ form. Crops that respond favorably to mixed N nutrition or enhanced NH_4^+ supply include barley (*Hordeum vulgare* L.; Leyshon et al., 1980); sorghum (*Sorghum bicolor* (L.) Moench; Camberato and Bock, 1989); wheat (*Triticum aestivum* L.; Camberato and Bock, 1990); maize (Below and Gentry, 1992); and Italian ryegrass (*Lolium multiflorum* Lam.; Alderman and Streeter, 1997). Unfortunately, this advantage of enhanced NH_4^+ supply has only infrequently been reported in field grown plants (Smiciklas and Below, 1992). Difficulty inhibiting nitrification to enhance NH_4^+ supply or positional availability of NH_4^+ may minimize the advantage to mixed N nutrition in field situations (Bock, 1986). Plants grown in soils where most of the N is derived from soil organic matter and plant residues and in acid or cold soils where nitrification is slowed may accumulate significant amounts of N in the NH_4^+ form without the aid of an artificial nitrification inhibitor. Otherwise, soils have little propensity to accumulate or store bioavailable NH_4^+-N (Chang et al., 1991; Muñoz et al., 2003).

11.1.4 Nitrogen Transformations Affecting Nitrogen Availability

Nitrogen bioavailability to nonleguminous plants is predicated in the presence of NH_4^+ and NO_3^- for root uptake. Thus, indigenous soil N, applied organic N, uric acid, urea, and other N-containing substances are only available to the plant after they are mineralized to NH_4^+ and NO_3^-. Nitrogen mineralization and immobilization (the microbial transfer of inorganic N to organic N) are discussed in detail in Section 27.2 of *Handbook of Soil Sciences: Properties and Processes*. Although NH_4^+ is subject to conversion to NH_3 in a high pH environment and volatilization to the atmosphere if on the soil surface, the loss of NH_4^+ from the soil is considerably less overall than the loss of NO_3^-. Unfortunately, the nitrification of NH_4^+ to NO_3^- (see Section 27.3 of *Handbook of Soil Sciences: Properties and Processes* for details) occurs readily in most soils and the subsequent loss of NO_3^- by leaching and denitrification substantially reduces N bioavailability.

11.1.4.1 Nitrogen Mineralization

The rate and extent of N mineralization determines the bioavailability of organic N sources, most importantly soil organic matter, crop residues, manures, and by-products of municipal waste treatment and industrial processes.

11.1.4.1.1 Soil Organic Matter

Stevenson (1982) reported that >90% of the N in soils is in the organic form. Organic N in the plowed layer of mineral soils ranges from 0.8 to 4.0 g N kg^{-1} (Bremner, 1965, p. 96) representing 1800–9000 kg N ha^{-1}. Thus, a 2% mineralization rate would provide 36–180 kg inorganic-N ha^{-1}, potentially a significant percentage of crop N accumulation. Cassman et al. (2002) determined indigenous N from maize uptake in 55 field experiments in the North-Central United States to typically range between 80 and 240 kg N ha^{-1}, with most providing between 100 and 140 kg N ha^{-1}. Predicting N bioavailability from soil organic N is important to increase the efficient use of fertilizer and added N and to decrease N losses to the environment (Cassman et al., 2002; Mulvaney et al., 2005). The importance of moisture and temperature (Stanford and Epstein, 1974; Kladivko and Keeney, 1987) and pH (Cornfield, 1952; Dancer et al., 1973; Olness, 1999) on N mineralization are well established. Unfortunately, laboratory tests of N mineralization have largely been unsuccessful (Griffin, 2008) in predicting N mineralization in the field, likely because most do not account for the impact of varying temperature and/or moisture in the field on N mineralization. Honeycutt et al. (1991) and Griffin and Honeycutt (2000) improved the incubation-based prediction of N mineralization from soil organic N, fertilizer, crop residue, sludge, and manure by including cumulative thermal units into equations based on soil properties and moisture.

11.1.4.1.2 Crop Rotation and Residue Effects on Nitrogen Bioavailability

Much effort has been placed on determining the cause of lower yield and higher N requirement in continuous maize compared to maize grown after soybean (*Glycine max* L.). Nitrogen availability is an important factor, although many other factors also contribute. Nitrogen uptake by maize grown after soybean in Wisconsin was 51 kg N ha^{-1}, greater than maize grown after maize on two silt loams, but no different in a sandy soil (Bundy et al., 1993). Nitrogen uptake of a second cereal crop grown 2 years after soybean was reduced to 36 kg N ha^{-1} (Vanotti and Bundy, 1995). The authors proffered that the second year reduction in N bioavailability was due to soybean removing more N from the soil than was fixed symbiotically as described by Heichel and Barnes (1984) and others (David et al., 1997; Jaynes et al., 2001). The yield benefit of maize grown after soybean, compared to maize grown after maize, was the same whether the soybean was nodulating or nonnodulating, and was not eliminated by the application of fertilizer N to a silt loam in Wisconsin (Maloney et al., 1999). These findings suggest that the "rotation effect" was not likely a result of N provided directly by the soybean crop, but an enhancement

in the maize plant's ability to accumulate and utilize N. However, Gentry et al. (2001), using a similar experimental approach including nodulating and nonnodulating soybean, had a different conclusion. The "rotation effect" was due both to a decrease in N mineralization in continuous maize and to an increase in soil N arising from symbiotic fixation in maize after soybean.

Alternatively, it has been suggested that the effects of crop residues on N bioavailability may arise from their effect on soil temperature. Normal amounts of corn residue or simulated residue lowered soil temperature 0.7°C–1.7°C and resulted in 32 kg ha^{-1} less N than when residues were removed (Andraski and Bundy, 2008). Since the simulated residue (polypropylene snow fence) had a similar effect on soil temperature and N availability as corn stover, it was concluded that temperature, not microbial immobilization, had altered N bioavailability. This seems plausible since only 3–5 kg ha^{-1} of soybean residue–derived N was taken up by maize grown the following season on two Mollisols in Kansas, even though 144–155 kg N ha^{-1} more N fertilizer had to be supplied to maize grown after maize to achieve the same yield as maize after soybean (Omay et al., 1998). Crookston et al. (1991) pontificated that the "rotation effect" was "a somewhat fickle and elusive phenomenon" and was "easier to exploit … than to explain." Twenty years later this statement is still true.

11.1.4.1.3 Cover Crop Effects on Nitrogen Bioavailability

Legumes grown as cover crops differ in N fixation and residual N accumulation (Heichel and Barnes, 1984). Conditions affecting the growth of a cover crop, such as moisture and temperature, also affect its N fixation and recovery of residual N, thereby affecting the potential N contribution to the subsequent crop. The rate and extent of N mineralization from the cover crops determine the bioavailability to the following crop, which is influenced by the composition of the cover crop, placement on or incorporation in the soil, moisture, and temperature. Plant tissue with high C:N and high concentrations of lignin, cellulose, and hemicelluloses decompose and release N slower than plants with lower levels of these constituents (Wagger et al., 1998).

Legumes can fix considerable amounts of N that are significant when compared to the uptake of the subsequent cereal crop. For example, in Delaware, hairy vetch (*Vicia villosa* Roth.) and crimson clover (*Trifolium incarnatum* L.) grown in combination with spring oats (*Avena sativa* L.) or cereal rye (*Secale cereale* L.) accumulated ≈117 kg N ha^{-1} more N in cover crop roots and shoots than when either cereal was grown alone (≈55 kg N ha^{-1}) (Mitchell and Teel, 1977). An average of 90% of the cover crop N was in the top growth and about 33% of the N was released to the following maize crop. Similarly in North Carolina, crimson clover and hairy vetch, compared to a fallow treatment, increased N recovery by the subsequent maize crop ≈42 kg N ha^{-1}; equivalent to about 33% of the aboveground N content of the cover crops (Wagger, 1989a). Cereal rye, in comparison to legume cover crops, reduced N recovery by about 25 kg N ha^{-1} compared to fallow—likely arising from the high C:N of the rye (≈35:1; Wagger, 1989b) and N immobilization. Hairy vetch, big flower vetch (*Vicia grandiflora* W. Koch), and crimson clover grown as winter cover crops in Kentucky accumulated 173, 24, and 20 kg N ha^{-1} more aboveground plant N than cereal rye (36 kg N ha^{-1}), respectively (Ebelhar et al., 1984). Poor growing conditions, including low rainfall, reduce N accumulation. Four cover crop systems grown in the Brazilian Cerrados contributed 25–64 kg N ha^{-1} to the following maize crop in one season, but had no effect in the second season in which cover crop growth and N uptake were reduced by dry weather (Maltas et al., 2009).

Date of planting (growing season length), killing date, and moisture affect N fixation and N recovery of cover crops. A late August planted wheat-hairy vetch mixture grown 30 km south of Vancouver, British Columbia produced 126 kg N ha^{-1}, whereas the same mixture planted 4 weeks later produced only 70 kg N ha^{-1} (Odhiambo and Bomke, 2001). Many researchers have focused studies on the impact of kill date on cover crop N accumulation (Wagger, 1989a, 1989b; Clark et al., 1994, 1997; Odhiambo and Bomke, 2001; Sainju and Singh, 2001). The longer the cover crop is allowed to grow, the greater the amount of N that is fixed or recovered from the soil. Hairy vetch and a vetch-cereal rye mixture accumulated ≈2 kg N ha^{-1} day^{-1} in the aboveground biomass form late March until early May in Maryland (Clark et al., 1997).

Temperature, moisture, and placement of cover crop residues affect N contribution of the cover crop to the subsequent main crop. For several cover crops, faster N mineralization occurred in the first year of a 2 year study, due to higher rainfall (79 versus 15 mm) and higher mean air temperature (29°C versus 25°C) in the first 4 weeks of residue decomposition in North Carolina (Ranells and Wagger, 1996). Nearly complete N release from the hairy vetch cover crop occurred twice as fast in year 1 than year 2, 8 versus 16 weeks. Incorporating legume cover crop residue into a *Typic Paleudalf* in Kentucky increased the rate and extent of N release to the following crop (Varco et al., 1989). Maize recovered 31 kg ha^{-1} more N when hairy vetch was incorporated into the soil compared to when left on the soil surface, 32% versus 20% of the residue N content, respectively.

Nonlegume cover crops can be effective at recovering residual N from a previous crop or a post-growing season manure application. Nitrogen accumulation and subsequent release to the following crop determine bioavailability and environmental impact. In an irrigated *Xeric Torripsamment* sand in eastern Washington, about 29% of the 92–142 kg N ha^{-1}, captured by a mustard (*Brassica hirta* Moench) cover crop from fertilizer applied to a winter wheat-sweet corn-sweet corn rotation was recovered by the following potato (*Solanum tuberosum* L.) crop (Collins et al., 2007).

Cover crops can increase N bioavailability by reducing percolation losses (Weinert et al., 2002) as well as by recovering residual N. An estimated 50% of the 9 cm of winter rainfall was used by cover crops grown on a *Xeric Torripsamment* in the Columbia Plateau of central Washington. Thus, soil mineral N was reduced by 155 kg N ha^{-1} to a depth of 180 cm by cereal rye, wheat, or rapeseed (*B. napus* L.). However, winter water use by cover crops can sometimes reduce yield and N recovery by the subsequent crop, particularly in semiarid regions (Unger and

Vigil, 1998). Bioavailability of cover crop N can be assessed by aboveground N accumulation, with the PSNT soil test for NO_3^- or NO_3^- and NH_4^+ (Vaughan and Evanylo, 1999), or growing degree day predictive methods (Schomberg and Endale, 2004).

11.1.4.1.4 Nitrogen Bioavailability from Animal Manure and Organic N Sources

The term "animal manure" is used to refer to the array of complex substances arising from animal feces, urine, bedding, unused ration, water, medications, and growth promoters. Organic substances used as N sources for crop plants include by-products from vegetable, meat, oilseed, starch and sugar processing, municipal waste treatment (sewage sludge or biosolids), paper manufacturing, and other processes. A thorough discussion of these by-products can be found in Power and Dick (2000). This section will concentrate on N bioavailability from animal manure, although the same principles apply to other organic N sources. Nitrogen forms in manure include NO_3^-, NH_4^+, NH_3, urea, uric acid, and complex organic N compounds. Managing and predicting N bioavailability from manures is more difficult than that from inorganic fertilizer because of the variable composition of these materials and practical considerations that foster less than optimum timing and placement. The transformations of these compounds as affected by application method, timing, soil cation exchange and buffer capacity, and weather determine N bioavailability, but are difficult to predict. Bioavailability estimates for manures generally include availability factors for N that consider inorganic N loss (primarily NH_3 volatilization and NO_3^- leaching), based on application method and timing and an estimate of organic N mineralization. Nitrogen bioavailability from manure may also be represented in terms of "fertilizer replacement value" or "fertilizer equivalency," which does not take into account N loss that both fertilizer and manure N would be subjected to equally.

Manure N availability algorithms for making manure application rate recommendations for 34 states were reviewed and programmed by Joern et al. (2009). They found that 27 different variables were used to determine plant-available manure N and that for any single state 5 to 12 variables are needed to make this determination. While the number of variables required is indeed large, once the manure source is determined, 12 states use only one factor (e.g., total manure N) and 15 states use only two factors (e.g., total manure N and application method) to determine plant-available manure N. All but one state include method of application to determine plant-available manure N; however, only 13 out of 34 states use month of application to determine manure N availability.

Pratt et al. (1973) developed the "decay series" concept to represent manure N bioavailability over multiple growing seasons. The yearly rates of N mineralization in a decay series are given as the fraction of total N (year 1) or residual N (year 2 and beyond) mineralized. For example, if manure were applied containing 100 kg N ha^{-1}, the decay series 0.35, 0.15, 0.10, and 0.05 would predict mineralized N of 35 kg ha^{-1} in year 1 (0.35 × 100 kg N ha^{-1}), 9.8 kg ha^{-1} in year 2 [0.15 × (100 − 35 kg N ha^{-1})], 5.5 kg ha^{-1} in year 3 [0.10 × (100 − 35 − 9.8 kg N ha^{-1})], and 2.5 kg N ha^{-1} in year 4 [0.05 × (100 − 35 − 9.8 − 5.5 kg N ha^{-1})]. Nitrogen bioavailability from successive annual applications of manure would include N mineralized from previous seasons as well as the current growing season. Thus, if manure containing 100 kg N ha^{-1} were applied annually, N bioavailability in year 4 of the previous example would be 52.8 kg ha^{-1} (35 + 9.8 + 5.5 + 2.5 kg N ha^{-1}). The term "mineralized" was used by Pratt et al. (1973) to represent inorganic N released from urea and uric acid as well as slowly mineralizable organic N. Although this concept was originally put forth to estimate actual mineralization, the author's first experimentally based decay series, 0.40, 0.25, 0.06 from a field trial in the Coachella Valley, California, was based on fertilizer equivalency. Not surprisingly, decay series were found to be soil dependent. Dairy manure N bioavailability determined in a 5 year Vermont study was lower on a somewhat poorly drained clay soil (decay series—0.35, 0.15, 0.10, 0.075, and 0.05) than on a well-drained loam soil (decay series—0.60, 0.15, 0.10, 0.075, and 0.05), perhaps due to denitrification losses in the year of application (Magdoff, 1978).

Plant-available N in poultry litter was estimated in incubation studies to be approximately 80% of the inorganic N and 60% of the organic N contents and this provided a reasonable estimate of N bioavailability in two field experiments with maize, conducted in sandy loam Ultisols in Delaware (Bitzer and Sims, 1988). Nitrogen recovered in the second growing season from the 280 kg organic N ha^{-1} added at the highest rate of poultry manure was equivalent to only 31 and 16 kg N ha^{-1} fertilizer N, 11% and 6% of the organic N applied. Camberato and Frederick (1994) found no difference in residual N from poultry manure and fertilizer N applied at comparable N rates. High N availability shortly after poultry manure application and little residual value suggest that poultry manure application timing should be similar to that recommended for inorganic fertilizer to avoid leaching and denitrification losses.

Swine manure is often handled as a slurry or liquid from a lagoon. In this form 60%–80% of the total N content is in the NH_3/NH_4^+ forms (Mikkelsen, 1997). Thus, NH_3 volatilization from surface applications affects bioavailability. Only 40% of the total N content of surface-applied liquid swine manure slurry is considered available in comparison to 70%, when incorporated. Rapid conversion of NH_4^+ to NO_3^- and subsequent leaching and denitrification losses would be similar to those incurred with NH_4^+ fertilizers. Swine manure lagoon sludges have a higher organic N content (75%), thus predicting that organic N mineralization is a main determinant of bioavailability.

Dairy manure has a higher C:N ratio and more organic N than poultry or swine manure. Net nitrification and immobilization from nine dairy manures was more accurately predicted by considering the impact of manure C or neutral detergent fiber on N transformations (Griffin et al., 2005). The fertilizer N equivalency of dairy manure organic N was determined from maize N accumulation in New York to be 21%, 9%, 3%, 3%, and 2% of the original organic N content in years 1–5 after application, respectively (Klausner et al., 1994).

11.1.5 Factors Reducing N Bioavailability

11.1.5.1 Nitrogen Immobilization

Nitrogen can be added to the soil, remain in the rootzone, yet be unavailable to the crop. Immobilization of inorganic N by microorganisms decomposing high C:N crop residues (>20–30:1), such as maize, oat, or wheat stover or other organic materials can render substantial quantities of inorganic N unavailable for periods of time (Alexander, 1977). Substances such as sawdust or other wood-based by-products can have an even greater effect on N bioavailability than crop residues. For example, a papermaking sludge with a C:N ratio of 480:1 immobilized soil N for at least 250 days when added at 267 g sludge kg^{-1} soil (Zibilske, 1987). Ammonium is preferentially used by heterotrophic microflora, but NO_3^- is also immobilized in the absence of NH_4^+ (Recous et al., 1990).

11.1.5.2 Conversion of Ammonium to Nitrate Increases the Potential for Nitrogen Loss

Losses of NH_4^+-N from soil are generally small but NO_3^--N can be lost in large quantities by leaching and denitrification. Thus, nitrification, the conversion of NH_4^+ to NO_3^- by *Nitrosomonas* and *Nitrobacter* (see Section 27.3 of *Handbook of Soil Sciences: Properties and Processes*), is a critical factor that determines N bioavailability in many situations. Many factors affect nitrification rate, including temperature, pH, and soil type.

In laboratory incubations the nitrification rates of four soils increased with increased temperature from near 0°C to 27°C or 35°C, dependent on soil type (Frederick, 1956). The rate of nitrification is increased by increased temperature, but can proceed at relatively high rates with low temperatures in some soils. For example, equal nitrification rates occurred in a clay loam Ultisol incubated at 32°C or 8°C, but only after a 6 week lag period at the lower temperature (Anderson and Boswell, 1964). Nitrification proceeded in a field study in Missouri as soil temperature approached 0°C, albeit at a reduced rate (Kidwaro and Kephart, 1998).

Low soil pH reduces nitrification rate. A fivefold difference in nitrification during a 15-day incubation at 23°C occurred across a range of pH from 4.5 to 6.5 in a *Typic Argiudoll* (Dancer et al., 1973). Liming an acid soil from 5.0 to 7.4 tripled nitrification during a 3–4 week incubation (Frederick, 1956). In Iowa field experiments, 89% nitrification of fall-applied anhydrous ammonia was achieved in mid-April in soils with pH > 7.5, but only 39% nitrification occurred in soils with pH < 6.0 (Kyveryga et al., 2004).

Nitrapyrin is an effective inhibitor of nitrification (Bundy and Bremner, 1973) that is commonly applied with NH_4^+-containing and NH_4^+-forming fertilizers and manure. The persistence of nitrapyrin ranges from 5 to 50 days and is dependent on soil texture, organic matter, and temperature (Keeney, 1980). The effectiveness of nitrapyrin is greater at lower temperature; therefore, it is often applied with fertilizer after soil temperatures fall below 10°C in autumn for a spring crop (Touchton et al., 1978). Dicyandiamide (DCD) is another commercially available nitrification inhibitor and slow-release N source (Amberger, 1981) that has greater mobility in soil than nitrapyrin. Surface applications of urea and DCD can be moved into the soil with irrigation, shortly after application; but this mobility can also result in separation of DCD from NH_4^+ after urea hydrolysis (Bock et al., 1981).

A nitrification inhibitor can be effective at increasing N bioavailability and reducing NO_3^- leaching and denitrification. Apparent N recovery by maize grown on a sand-textured Ultisol in North Carolina was increased from 17% to 53% by including a nitrification inhibitor with urea versus urea alone (Chancy and Kamprath, 1982). After 22 cm rainfall, substantially more N remained in the upper 55 cm of soil 48 days after application with the nitrification inhibitor, than without. Similarly in a Minnesota study, applying a nitrification inhibitor with urea at 134 kg N ha^{-1} just prior to planting increased maize grain yield 28% on a loamy coarse sand with an available water holding capacity of only 7 cm m^{-1} (Malzer, 1989). Rainfall during the 8 weeks after application averaged 21.5 cm for the 3 years of the study, likely causing substantial NO_3^- leaching when urea was applied without a nitrification inhibitor.

Nitrification inhibitors affect N loss via denitrification as well as via leaching. Bioavailability of fertilizer N applied to a clay loam Ultisol increased when nitrapyrin was added with the fertilizer due to a decrease in denitrification (McElhannon and Mills, 1981). Nitrification of NH_4^+-N in liquid swine manure was complete in 7 weeks without a nitrification inhibitor, but was delayed up to 15 weeks with inclusion of 50 mg nitrapyrin active ingredient per liter of manure (McCormick et al., 1983). Increased N bioavailability was attributed to reduced denitrification as little NO_3^--N was found below the bands of untreated manure.

11.1.5.3 Nitrogen Leaching Reduces Nitrogen Bioavailability

Leaching of NO_3^- from the soil reduces bioavailability to plants and impacts environmental quality. Excess N in surface waters contributes to eutrophication (Keeney and Hatfield, 2008). High NO_3^- and nitrite (NO_2^-) in drinking water and food can cause methemoglobinemia in humans and animals (National Research Council, 1972).

The amount, intensity, and timing of rainfall, evapotranspiration, soil N levels, and many other factors impact the amount of N lost by leaching. In fertilized and manured soils the timing of N uptake by crops in relation to N application and rainfall exceeding evapotranspiration are key factors (Watts and Hanks, 1978). Nitrate movement in sandy soils is thought to occur more or less through the entire soil matrix and, thus, is envisioned as moving downward with the wetting front in proportion to rainfall in excess of evapotranspiration. Nitrogen loss can be substantial and rapid. In structured soil, water moves through an incomplete volume of the soil matrix; thus, NO_3^- is lost from the soil proportional to its concentration and much more slowly and less completely than in sand-textured unstructured soils.

In dry climates and on heavy-textured soils, NO_3^- leaching is limited. Only 7 kg NO_3^--N ha^{-1} $year^{-1}$ of 168 kg N ha^{-1} applied to

a field continuously cropped to maize was found in subsurface discharge from loess soils in Iowa (Burwell et al., 1976). Thus, N applied to one crop can "carryover" and be accumulated by the next crop. For example, carryover of fertilizer N from 168 kg N ha^{-1} N applied for maize on a silt loam soil in Wisconsin was about 50% of that applied, ranging from 32 to 106 kg N ha^{-1} using oat to estimate bioavailability (Vanotti and Bundy, 1994). Residual N was highest when N uptake of the maize was reduced by dry weather. Thus, soil NO_3^- testing is often recommended for adjusting N rate recommendations in dry climates (Section 13.2).

In contrast, N leaching occurs readily in warm humid climates on sandy soils, with irrigation, and in heavier-textured soils that are tile drained. A total of 161 kg N ha^{-1} NO_3^--N was leached below 120 cm soil depth in a sandy loam Hapludoll that was irrigated with 50 mm of water each time available soil water decreased to about 50 mm (50% depletion) (Timmons, 1984). Leaching of NO_3^--N from a split application of 185 kg N ha^{-1} beyond 152 cm soil depth in a loamy fine sand Haplustalf was increased by irrigation, 25% above optimum, about 60 mm $year^{-1}$ (Gehl et al., 2005). Only about 10% of the 168 kg N ha^{-1} applied to maize was recovered by wheat (Camberato and Frederick, 1994) or a cereal rye and annual ryegrass (*L. multiflorum* Lam.) cover crop (Shipley et al., 1992).

Nitrate-N leaching occurs in heavier-textured soil if tile drained. Nitrogen leaching ranged from 13 to 61 kg NO_3^--N ha^{-1} $year^{-1}$ in a maize–soybean rotation on Mollisols in Iowa and from 15 to 38 kg N ha^{-1} $year^{-1}$ in silt loam Alfisol (Jaynes et al., 2001). Annual NO_3^--N loss from a tile-drained silt loam *Typic Glossaqualf* in Indiana decreased from 38 to 15 kg N ha^{-1} by including soybean in rotation with corn, reducing N application from ≈300 to ≈200 kg N ha^{-1}, and planting a winter wheat "catch crop" after corn in the rotation (Kladivko et al., 2004). Nitrate leaching from maize grown on Coastal Plain soils in Maryland was reduced to 80% by cereal rye cover crop (Staver and Brinsfield, 1998). Field-scale watershed studies suggested that groundwater NO_3^- was reduced to 60% by the use of cereal rye cover crops.

The environmental benefit of a cover crop is dependent on when the N is mineralized and nitrified and how much is utilized by the subsequent crop. Even though forage and oilseed radish (*Raphanus sativus* L.) were as effective as rapeseed and cereal rye in recovering N from the previous crop, the captured N was released earlier in the spring in Maryland due to winter kill (Dean and Weil, 2009). Thus, high pore water NO_3 in the soil profile under the radishes suggested leaching of NO_3^- from the loamy sand soil was possible unless followed by an early-planted spring crop. Frost-sensitive crops, sudangrass (*S. bicolor* L.) and white mustard, also released N prematurely resulting in soil NO_3^- levels higher than bare fallow (Weinert et al., 2002).

Anion exchange capacity originating at low pH in weathered Alfisols, Ultisols, and Oxisols may slow NO_3^--N loss (Toner et al., 1989; Eick et al., 1999); however, the ability of plants (particularly crop plants) to root into these acid soil layers is questionable due to low Ca availability and/or Al toxicity (Adams and Lund, 1966; Adams and Moore, 1983).

Nitrogen fertilizer, primarily anhydrous ammonia, is often applied in relatively cold and dry climates in late fall for a crop to be planted the following spring. Although nitrification may be limited just after application due to cold soil temperatures, significant nitrification can occur in the spring as the soils warm. Substantial N loss due to leaching and/or denitrification can occur prior to crop N demand. For example, in a corn–soybean rotation, apparent N recovery of anhydrous ammonia applied for corn on a tile-drained Mollisol in southern Minnesota was only 45% for fall-applied N compared to 87% for spring-applied N (Vetsch and Randall, 2004). Nitrate-N loss to tile drainage in this environment was reduced to 14% by spring application in comparison to fall-applied N (Randall and Vetsch, 2005).

11.1.5.4 Denitrification Reduces Nitrogen Bioavailability

Denitrification, conversion of NO_3^- to N_2 or less reduced gaseous N forms (see Section 27.4 of *Handbook of Soil Sciences: Properties and Processes* for details), lowers N bioavailability and contributes to greenhouse gas emissions and global warming. Denitrification losses increase with increasing temperature, but denitrification will occur in winter months with losses to the atmosphere occurring upon thawing (Dusenbury et al., 2008). Anaerobic conditions promote denitrification as do near-neutral soil pH, increasing NO_3^--N (McSwiney and Robertson, 2005; Millar et al., 2010) and soluble C.

Denitrification losses can be agronomically as well as environmentally important on poorly drained soils, with irrigation, application of manures or organic by-products, or reduced tillage. Denitrification losses were substantial on a clay (770 g kg^{-1}) *Typic Humaquept* near Québec City, Canada, on which barley was grown over a 3 year period, ranging from 12 to 45 kg N ha^{-1} during the snow-free season (Rochette et al., 2007). No-tillage, in comparison to moldboard plowing, resulted in a 2.5-fold increase in denitrification due to an increase in water-filled pore space. Denitrification losses in a well-drained loam soil in the same catena as the clay soil were ≤1.5 kg N ha^{-1}. Well-drained soils in dry climates have relatively low denitrification losses. Cumulative denitrification N loss over a 2 year period from four cropping systems in the semiarid northern Great Plains ranged from 0.3 kg N ha^{-1} for alfalfa (*Medicago sativa* L.)-perennial grass to 1.3 kg N ha^{-1} for continuous wheat (Dusenbury et al., 2008).

High rates of N_2O flux from the soil, 0.24–1.06 kg N ha^{-1} day^{-1}, occurred from three vegetable production systems in Santa Barbara County, California (Ryden and Lund, 1980). Peak N_2O emissions followed the first furrow irrigation after N fertilization. Annual emissions were estimated to range from 20 to 42 kg N ha^{-1}. Organic materials high in bioavailable C that stimulate microbial respiration may create an anaerobic microenvironment, creating conditions suitable for denitrification (Rice et al., 1988).

Greater denitrification occurred with alkaline-hydrolyzing fertilizers, anhydrous ammonia, and urea, in comparison to acidic fertilizers, because of increased soil pH and water soluble organic carbon with the alkaline fertilizers (Mulvaney et al., 1997).

Denitrification losses of N from banded urea fertilizer (applied at 218 kg N ha^{-1}) for maize grown on a furrow irrigated, well-drained Aridic Argiustoll in Colorado were 3.2 and 1.7 kg N ha^{-1} in each year of the study (Bronson et al., 1992). Peak N_2O emissions were coincident with irrigation and rainfall and were reduced by slowing the conversion of urea to NO_3^- by including the nitrification inhibitor, nitrapyrin, with the banded fertilizer. Cumulative denitrification N losses from maize grown with 210 kg N ha^{-1} as surface-applied urea, no-tillage, and sprinkler irrigation on two Mollisols in Argentina were 9.8 and 2.1 kg N ha^{-1}, for preplant and sidedress N application, respectively (Sainz Rozas et al., 2001). Most of the N loss occurred when water-filled pore space exceeded 80%.

11.1.5.5 Ammonia Volatilization Reduces Nitrogen Bioavailability

Volatilization of NH_3 from fertilizer and manure can be substantial, easily >25% of the N content of several fertilizer and manure sources (Lauer et al., 1976; Fillery et al., 1984). Direct loss of anhydrous ammonia and aqua ammonia fertilizers can occur through improper soil application (Parr and Papendick, 1966) or application in irrigation water (Gardner and Roth, 1984). Ammonia losses can also occur from fertilizers that do not initially contain NH_3 if they are left on or near the soil surface and conditions are suitable for conversion of NH_4^+ to NH_3. pH and temperature are the two primary factors affecting NH_3 loss. Increasing pH increases NH_3 volatilization because it increases the proportion of ammoniacal-N in the NH_3 form (du Plessis and Kroontje, 1964).

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O \quad (11.1)$$

Increasing temperature increases the driving force for NH_3 volatilization by decreasing the pK_a for the equilibrium (Koelliker and Kissel, 1988). Wind also increases NH_3 loss (Fillery et al., 1984), as long as it does not impede urea hydrolysis by drying the reaction site.

11.1.5.5.1 Ammonia Volatilization from Fertilizers

Ammonium sulfate or $(NH_4)_2HPO_4$ application to calcareous soils can result in substantial NH_3 loss (Fenn and Kissel, 1973). However, when applied to lower pH soils most NH_4^+-containing fertilizers result in little NH_3 volatilization (Volk, 1959). In contrast, NH_3 volatilization is likely with urea-containing fertilizers in many situations because urea hydrolysis increases pH (Overrein and Moe, 1967) as NH_4^+ is formed.

$$CO(NH_2)_2 + H^+ + 2H_2O \rightarrow 2NH_4^+ + HCO_3^- \quad (11.2)$$

Low buffer capacity soils result in greater NH_3 volatilization due to greater increases in pH and lower retention of exchangeable NH_4^+ (Ferguson et al., 1984).

Ammonia volatilization losses from urea are higher when applied to crop residues (e.g., no-tillage cropping systems), pasture, or turfgrass in comparison to the soil surface, partly because residues and plant tissues have high urease activity (Torello and Wehner, 1983; Dick, 1984), resulting in rapid urea hydrolysis and substantial pH changes on low buffered materials (McInnes et al., 1986). Increased temperature promoted urea hydrolysis (Broadbent et al., 1958; Fisher and Parks, 1958) as well and also increased the proportion of ammoniacal-N in the NH_3 form (Koelliker and Kissel, 1988). Moisture is required for urea hydrolysis to occur (Ernst and Massey, 1960), but losses are enhanced as drying concentrates the NH_4^+ (Hargrove et al., 1977; McInnes et al., 1986). Rainfall of 28 and 33 mm incorporated urea into the soil and halted NH_3 volatilization, whereas irrigation of 2.5 mm increased loss (McInnes et al., 1986). Irrigation or rainfall amount must be sufficient to incorporate the N into the soil so as not to enhance losses (Kissel et al., 2004).

Fertilizer application method and form can affect NH_3 volatilization. Surface application of urea-containing fertilizers greatly enhanced NH_3 volatilization as determined by crop response (Mengel et al., 1982; Touchton and Hargrove, 1982; Fox and Piekielek, 1987). Hargrove (1988) suggested that a depth of 5–10 cm would prevent NH_3 loss from urea on most soils. Banding urea versus a broadcast application generally reduces NH_3 losses as well. Including a urease inhibitor (Schlegel et al., 1986), coating (Matocha, 1976), or encapsulating urea (Knight et al., 2007) also reduce NH_3 volatilization.

11.1.5.5.2 Ammonia Volatilization from Manures

Nitrogen applied to surface-applied manures is subject to NH_3 volatilization losses because potentially volatile N compounds are a significant percentage of the total N content. Urea comprised nearly 70% of the N in urine from ruminants (Bristow et al., 1992). Approximately 30%–50% of the total N content of various poultry manures was uric acid- and urea-N (Nicholson et al., 1996; Fujiwara and Murakami, 2007). Manure pH, which fosters NH_3 and enhances volatilization, may exceed 8.0 (Nicholson et al., 1996), greatly reducing N availability from poultry manures. Nearly 100% of the initial NH_4^+-N content of a poultry litter was lost by NH_3 volatilization in ≈8 days after application in summer when conditions were hot, dry, and windy (Sharpe et al., 2004). However, NH_3 loss in winter was only 10% of the NH_4^+-N content. Rainfall shortly after manure application to the soil surface reduces NH_3 volatilization by transporting volatile N forms into the soil (Cabrera and Vervoort, 1998; Sharpe et al., 2004). Ammonia loss from surface-applied cattle slurry, which was not incorporated, exceeded 40% of the initial NH_4^+-N content, but immediate incorporation with disk harrow, chisel plow, or moldboard plow substantially reduced loss to 5%, 9%, and 1%, respectively (Thompson and Meisinger, 2002). Peak NH_3 loss occurs soon after application (Marshall et al., 1998), so rainfall must also occur soon after application to be effective in reducing NH_3 volatilization.

11.1.5.5.3 Ammonia Volatilization from Plant Tissues

Ammonia volatilization directly from plant tissues can be substantial. Harper et al. (1987) estimated that 21% of the 73 kg ha^{-1}

fertilizer N applied in the spring of the year in Georgia was volatilized from wheat tissue. Direct volatilization of NH_3 from maize tissues in Nebraska was equivalent to 10%–20% of the fertilizer N applied, and apparent total N losses from aboveground plant tissues ranged from 45 to 81 kg N ha^{-1} (Francis et al., 1993). This loss was equivalent to 50%–75% of the unaccounted-for N in ^{15}N balance calculations. Although the results of these studies suggest NH_3 volatilization from plant tissue is substantial, rarely is this loss mechanism considered or quantified in N studies.

11.1.6 Ammonium in the Interlayer of 2:1 Clay Minerals

Ammonium ions occur in the interlayer of 2:1 clay minerals, particularly vermiculite and degraded illite (Nommik and Vahtras, 1982). Often, this phenomenon is referred to as "fixation," implying zero bioavailability. In reality, however, interlayer NH_4^+ exchanges with the soil solution to some degree and is, therefore, available for plant uptake. Fixation of nearly 10 mg kg NH_4^+-N (10% of that added as $(NH_4)_2SO_4$) occurred in less than 1 day in two vermiculitic soils (Broadbent, 1965). Green et al. (1994) found up to 23% of the N applied in urea was fixed as NH_4^+ after 20 days of anaerobic incubation. However, nearly half the fixed NH_4^+ was released during nitrification after 15 days of aerobic incubation (Green et al., 1994). Plant (Li et al., 1990) and microbial (Kelley and Stevenson, 1987) utilization of solution NH_4^+ also resulted in the release of fixed NH_4^+.

11.1.7 Predicting Nitrogen Bioavailability

Blackmer (1999) outlined many indices of N bioavailability; including Mitscherlich "b" and "c" values, Fried and Dean "A" values, Dean "a" values, and several biological and chemical tests for estimating N mineralization. Sims (Chapter 13) overviewed several inorganic N bioavailability tests including the residual inorganic N, preplant soil profile nitrate (PPNT), and the presidedress soil nitrate (PSNT) tests. The recently developed Illinois soil nitrogen test (ISNT), a purported indicator of mineralizable N, was also discussed by Sims. Girma and Raun (Chapter 15) discussed the use of optical sensors to make in-season estimates of N bioavailability by assessing crop canopy size and greenness. Tissue testing and hand-held chlorophyll meters were the precursors to optical sensors (Schepers et al., 1992) and achieved much the same goal. *Adapt-N* is a promising web-based tool used to make N recommendations for maize in New York that dynamically simulates the impact of weather on N transformations and transport to estimate crop N accumulation and predict N need (Melkonian et al., 2008). Given the complexity of the N cycle, the importance of temperature and moisture in affecting N bioavailability, and the economic and environmental costs of errors in N management, it is no wonder a sophisticated tool such as *Adapt-N* is needed to predict N bioavailability and improve N management.

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11.2 Phosphorus Availability

Andrew Sharpley

11.2.1 Introduction

Phosphorus (P) is an essential nutrient for plant growth. The low concentration (100–3000 mg P kg^{-1}) and solubility (0.01–0.10 mg P L^{-1}) of P in soils, however, make it a critical nutrient limiting plant growth. In natural ecosystems, P availability in soil is controlled by the sorption, desorption, and precipitation of P released during weathering and dissolution of rocks and minerals of low solubility. Thus, soil P availability is generally inadequate for crop needs in production agriculture. To meet these needs, P is added as fertilizers or animal manures to buildup or maintain soil P availability at predetermined optimum levels. In this section, P availability is defined as that P in soil or water that is available by desorption and dissolution processes for uptake by plants in terrestrial and aquatic ecosystems.

The components, forms, availability, and cycling of P in soil are conceptualized in Figure 11.1. Complex and interrelated processes determine the amounts and availability of several inorganic and organic forms of P in soil. This section will describe these processes occurring in the soil, how they are affected by agricultural management, how we attempt to optimize soil P availability for crop production, and how this can affect water quality.

11.2.2 Forms and Amounts in Soil

Soil P exists in inorganic (P_i) and organic (P_o) forms (Figure 11.1). Inorganic P forms are dominated by hydrous sesquioxides,

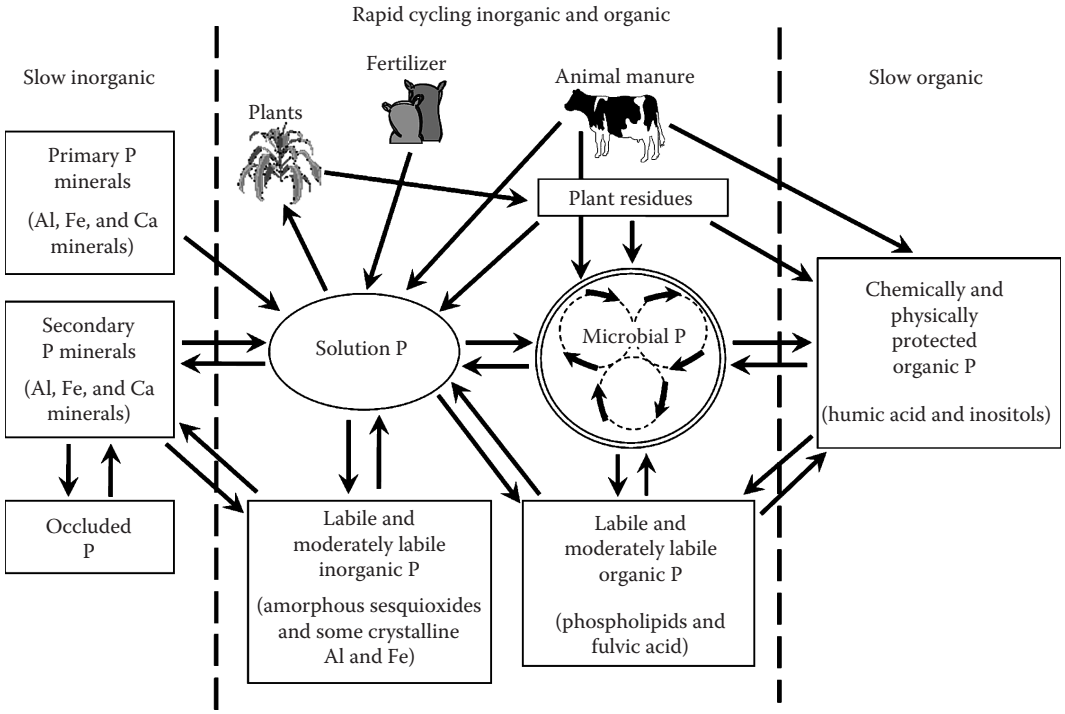

FIGURE 11.1 The soil P cycle: its components, forms, and flows. (Adapted from Stewart, J.W.B., and A.N. Sharpley. 1987. Controls on dynamics of soil and fertilizer phosphorus and sulfur, p. 101–121. *In* R.F. Follett, J.W.B. Stewart, and C.V. Cole (eds.) Soil fertility and organic matter as critical components of production systems. Soil Science Society of America Special Publication No. 19. ASA, CSSA, SSSA, Madison, WI.)

amorphous, and crystalline Al and Fe compounds in acidic, noncalcareous soils, and by Ca compounds in alkaline, calcareous soils (Figure 11.1 and Table 11.1). Organic P forms include relatively labile phospholipids and fulvic acids; more resistant forms comprise inositols and humic acids (Figure 11.1). Forms generalized in Figure 11.1 are not discrete entities, as intergrades and dynamic transformations between forms occur continuously to maintain equilibrium conditions. These approximated forms of P are assigned based on the extent to which sequential extractants of increasing acidity or alkalinity can dissolve soil P (Hedley et al., 1982; Tiessen and Moir, 2007; Zhang and Kovar, 2008).

TABLE 11.1 Average Amounts of Inorganic P (P_i) and Organic P (P_o) in the A1 Horizon of Virgin Calcareous, Slightly Weathered, and Highly Weathered Soils

	Calcareous (n = 41)	Slightly Weathered (n = 40)	Highly Weathered (n = 39)
P Form		(mg kg^{-1})	
Bioavailable P_i[a]	11	21	22
Amorphous Al and Fe-P_i	37	74	109
Ca-P_i	285	85	16
Labile P_o	8	18	34
Protected P_o	28	60	78
Residual P[a]	152	254	179
Total P	521	512	438

Source: Adapted from Sharpley, A.N., H. Tiessen, and C.V. Cole. 1987. Soil phosphorus forms extracted by soil tests as a function of pedogenesis. Soil Sci. Soc. Am. J. 51:362–365.

[a] Bioavailable P_i is resin P_i and residual P is chemically resistant, mineral, and occluded P_i and P_o as designated on Figure 11.1.

In most soils, the P content of surface horizons is greater than subsoil, due to the sorption of added P and greater biological activity and accumulation of organic material in surface layers. However, soil P content varies with parent material, extent of pedogenesis, soil texture, and management factors, such as rate and type of P applied and soil cultivation. These factors also influence the relative amounts of P_i and P_o. In most soils, 50%–75% is P_i, although this fraction can vary from 10% to 90% (Table 11.1). Generally, Ca-P_i decreases with weathering, whereas amorphous Al and Fe-P_i and P_o forms tend to increase, due in part to changes in soil clay fraction from basic primary minerals to Al- and Fe-dominated oxides (Table 11.1).

Phosphorus additions are usually needed to maintain adequate available soil P for plant uptake. The level of these additions varies with both soil and plant type (Pierzynski and Logan, 1993). Once applied, P is either taken up by the crop, becomes weakly (physical) or strongly (chemical) adsorbed onto Al, Fe, and Ca surfaces, or incorporated into organic P (McLaughlin et al., 1988; Ottabong et al., 1997; Zhang and MacKenzie, 1997) (Figure 11.2). As P_i generally supplies most of the P taken up by crops in productive agricultural soils, more attention has been focused on the availability of P_i rather than P_o, following P additions.

Overall, soil pH is the main property controlling the nature of P_i forms, although Al, Fe, Mn, and Ca content determine the

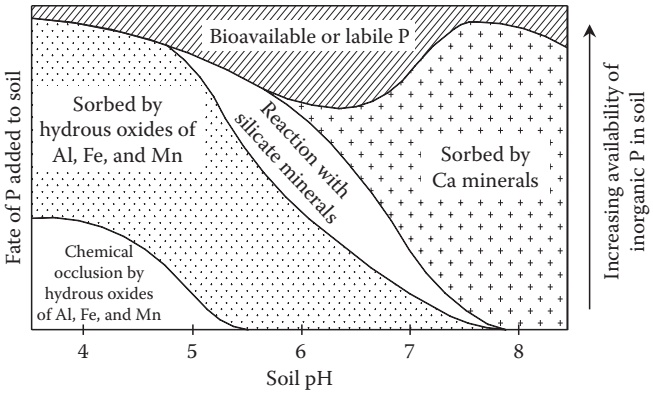

FIGURE 11.2 Approximate representation of the fate of P added to soil by sorption and occlusion in inorganic forms, as a function of soil pH. (Adapted from Buckman, H.O., and N.C. Brady. 1970. The nature and properties of soils. The Macmillan Publishing Co., Collier-Macmillan Limited, London, U.K.)

amounts of these forms (Figure 11.2). In acid soils, amorphous and hydrous oxides of Al, Fe, and Mn dominate P sorption processes, while Ca compounds dominate P sorption and precipitation reactions in alkaline soils. As a result, P availability is greatest at soil pH between 6 and 7 (Figure 11.2). Immobilization of P_i by these processes renders a portion of the added P unavailable for plant uptake (Figure 11.3). Mehlich-3 soil P decreased with time after application of P to a Kingsbury clay (*Aeric Ochraqualfs*; pH of 5.7) and Hagerstown silt loam (*Typic Hapludalfs*; pH of 6.8) incubated at room temperature (25°C) and field moisture (about 30% water). At the same time, P_i becomes more tightly bound with Al and Fe complexes (Figure 11.3). This simple soil-P incubation illustrates why the removal of P_i from soil by crops is generally low. For the United States, an average 29% of P added in fertilizer and manures is removed by harvested crops, ranging from <1% in Hawaii to 71% in Wyoming (National Research Council, 1993). The low recovery reflects the predominance of high P fixing soils in Hawaii.

Even though P_i has generally been considered the major source of plant-available P in soils, the mineralization of labile P_o has also been shown to be important in both low-fertility and high-fertility soils (Stewart and Tiessen, 1987; Oehl et al., 2001; Chen et al., 2002; Condron et al., 2005). Amounts of P_o mineralized in temperate dryland soils range from 5 to 20 kg P ha^{-1} $year^{-1}$ (Stewart and Sharpley, 1987). Mineralization of soil P_o tends to be higher in the tropics (67 to 157 kg P ha^{-1} $year^{-1}$), where distinct wet and dry seasons and higher soil temperatures enhance microbial activity. In contrast, P_o compounds may also become resistant to hydrolysis by phosphatase through complexation with Al and Fe (Tate, 1984).

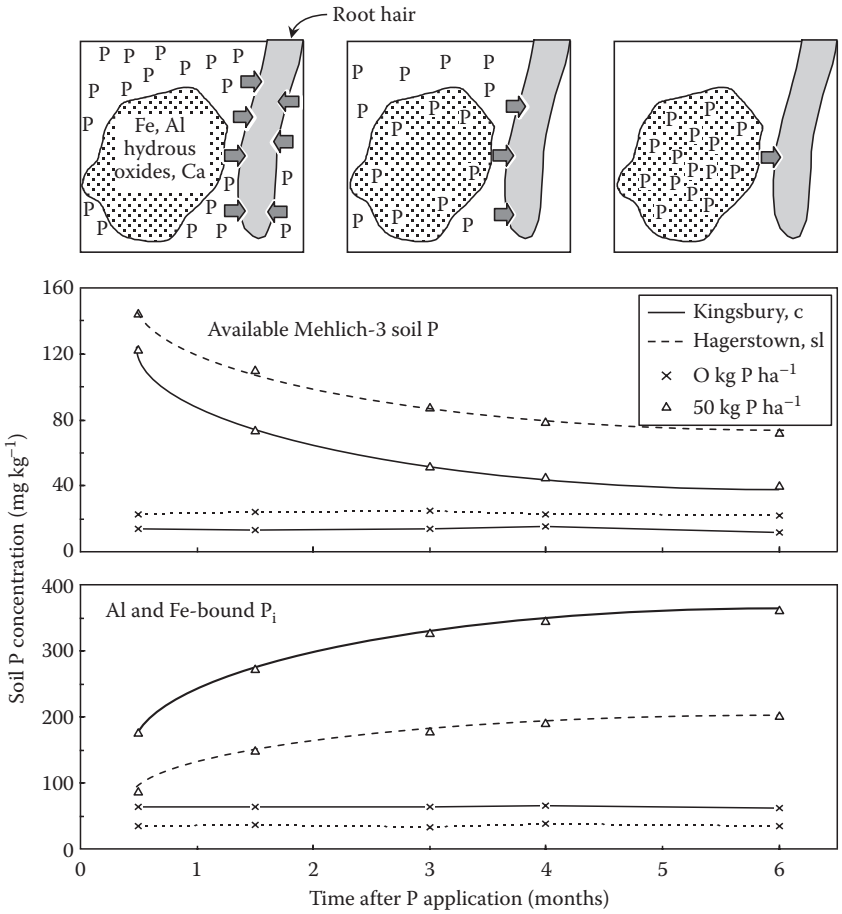

FIGURE 11.3 The change available (Mehlich-3 P) and adsorbed soil P (Al- and Fe-bound) with time after application of P.

11.2.3 Principles of Analysis

The various forms and amounts of P_i and P_o in soil can be estimated by extraction with acids and alkalies that dissolve specific complexes binding P. The most common methods and their background are given by Olsen and Sommers (1982), Turner et al. (2005), Tiessen and Moir (2007), Kovar and Pierzynski (2008). A wide range in methods and principles exists for effective recovery of P based on soil type, environment, and level of detail required. This is particularly true for available soil P_i estimation, which has traditionally been based on acid dissolution (acetic, citric, hydrochloric, lactic, nitric, and sulfuric), anion exchange (acetate, bicarbonate, citrate, lactate, and sulfate), cation complexation (citrate, fluoride, and lactate), or cation hydrolysis (buffered bicarbonate). Several excellent reviews of these methods are available for further reading (Kamprath and Watson, 1980; Fixen and Grove, 1990). In the United States, the most common soil P tests have been Mehlich-1 (Mehlich, 1953), Bray-1 (Bray and Kurtz, 1945), and Olsen P (Olsen et al., 1954); however, most laboratories have converted to the multielement Mehlich-3 (Mehlich, 1984) or AB-DTPA (Soltanpour and Schwab, 1977) extractants, in the past decade (Carter and Gregorich, 2007; Sims, 2008).

It is unlikely that an extractant would exclusively measure a single pool of soil P_i, although some components of extractants are aimed at specific pools. For example, F in the Bray-1 extractant exchanges with Al-bound P_i, with the assumption that this Al-bound P_i contributes to available P in acid soils, while the inclusion of EDTA in Mehlich-3 means this extractant estimates P associated with Fe and Al amorphous complexes. The success of any extractant to estimate available P depends on the appropriateness of the chemical used relative to dominant soil properties controlling P reactivity. Alternative methods utilize P-sinks, such as anion-exchange resins (AER), ion-exchange membranes, and Fe-oxide impregnated paper, to determine the quantity of soil P available to plants with negligible chemical extraction (Sharpley et al., 1994). These methods more closely mimic rhizosphere conditions and often provide comparable or better correlations with crop response than chemical extractants (Table 11.2).

11.2.3.1 Anion-Exchange Resins

AER are the most common P-sink method for assessing available soil P_i. The procedure typically involves the use of chloride saturated resin at a 1:1 resin-to-soil ratio in 10–100 mL of water or weak electrolyte for 16–24 h (Amer et al., 1955; Olsen and Sommers, 1982). To prevent the diffusion of P from the soil to the resin from being the rate-limiting step, resins should be intimately mixed with the soil, which creates difficulties in separating resin from soil for P analysis. Soil can be ground to a smaller size than the resin, but this probably changes soil P release characteristics. Resin and soil may also be separated by enclosing the resin in a mesh bag, which may limit resin–soil contact or float resin from soil in a sucrose solution (Thien and Myers, 1991). Skogley et al. (1990) encapsulated a mixture of anion- and cation-exchange resins in a mesh sphere. Greenhouse studies indicated that the correlation between P uptake by sorghum-sudangrass and resin-sphere results were as good or better than those with the Olsen P soil test (Table 11.2).

11.2.3.2 Ion-Exchange Membranes

A similar approach using ion-exchange resin impregnated membranes has been investigated by several researchers (Abrams and Jarrell, 1992; Qian et al., 1992; Saggar et al., 1992). Impregnation of the resin onto a plastic membrane facilitates separation of the resin beads from the soil and may eliminate the soil grinding step. Also, an extraction time as short as 15 min can be used, without reducing the accuracy of predicted P availability for a wide range of soils (Qian et al., 1992). In pot studies, the resin membranes have provided a better index of P availability than conventional chemical extraction methods for canola and ryegrass (Table 11.2).

11.2.3.3 Iron-Oxide Impregnated Paper

Another P sink that has received attention is Fe-oxide impregnated filter paper (Fe–O strip), which has successfully estimated available P_i in a wide range of soils and management systems (Menon et al., 1989b, 1990; Sharpley, 1991; Chardon, 2008) (Table 11.2).

Wide-spread adoption of P-sink methods for routine soil testing has not yet occurred in the United States, although parts of Brazil have used the method for the last decade (van Raij et al., 1986). As the P-sink methods operate with limited chemical extraction, they are more suited to a wide range of soils, irrespective of management history (Yang et al., 1991; Qian et al., 1992; Somasiri and Edwards, 1992; Myers et al., 2005). Where fertilizer history is unknown and frequent changes in fertilizer type, including rock phosphate, may have been made, it is difficult to choose the appropriate soil test. For example, Olsen P can underestimate and Bray-1 P overestimate P availability in soils amended with rock P, while P-sink methods have provided accurate estimates when KCl rather than $CaCl_2$ is used as the support medium (van Raij et al., 1986; Menon et al., 1989a; Saggar et al., 1992). Even so, detailed field calibration and improvement in standardized methodology will be essential before any of the P-sink approaches can be used routinely to estimate available soil P and make reliable fertilizer recommendations.

Phosphorus isotopes P^{32} and P^{33} have also been widely used to characterize soil P availability. Using laboratory incubation, greenhouse pot, and limited field plot studies, valuable insights have been gained into soil P availability in terms of exchange kinetics, plant-available forms, and the rate, extent, and direction of P cycling in soils. Readers are directed to excellent reviews by Fardeau et al. (1996), Di et al. (1997), and Frossard and Sinaj (1997) for more information.

11.2.4 Cycling in Soil

Dynamic processes involved in P cycling are chemical and biological (Figure 11.1). Chemical processes include precipitation–dissolution and sorption–desorption. Biological processes involve immobilization–mineralization initiated by P uptake

TABLE 11.2 Relationship between Crop Uptake of P and Bioavailable Soil P Determined by P Sink and Chemical Extraction

Crop	Location	Number of Soils	Soil P Test	Correlation Coefficient	Reference
Canola	Saskatchewan	135	IEM	0.92	Qian et al. (1992)
			Olsen	0.87	
Cotton	Brazil	28	AER	0.85	van Raij et al. (1986)
			0.02 M H_2SO_4	0.68	
Maize	Alabama, USA	32	Fe–O strip	0.87	Menon et al. (1989b)
			AER	0.62	
			Olsen	0.81	
			Bray 1	0.74	
Maize[a]	Australia	2	Fe–O strip	0.91	Kumar et al. (1992)
			IEM	0.91	
			Bray 1	0.87	
Maize	Egypt	10	Fe–O strip	0.90	Monem and Gadalla (1992)
			Olsen	0.91	
Maize	Uganda	2	Fe–O strip	0.85	Butewaga et al. (1996)
			Bray 1	0.77	
			Mehlich 1	0.64	
Rice	Brazil	8	AER	0.98	van Raij et al. (1986)
			AB-DTPA	0.41	
Ryegrass[a]	New Zealand	56	IEM	0.92	Saggar et al. (1992)
			Olsen	0.87	
Ryegrass	Finland	32	Fe–O Strip	0.93	Yli-Halla (1990)
			Olsen	0.87	
Sudangrass	Colorado, USA	23	AER	0.92	Bowman et al. (1978)
Sorghum/barley			Olsen	0.88	
WheatI	Australia	2	Fe–O strip	0.96	Kumar et al. (1992)
			IEM	0.97	
			Bray 1	0.98	
Wheat	China	39	Fe–O Strip	0.84	Lin et al. (1991)
			AER	0.83	
			Olsen	0.83	
			Bray 1	0.56	

Note: AEM, anion–exchange membrane; IEM, ion–exchange resin; AB-DTPA, ammonium bicarbonate diethylene triamine pentaacetic acid; PST, resin phytoavailability soil test.

[a] Relationship between relative crop yield and soil P test.

and decay of plants. Also, soil faunal and floral activities often modify the direction, extent, and rate at which these chemical and biological processes occur.

11.2.4.1 Chemical Processes

Precipitation–dissolution processes differ from sorption–desorption in that the solubility product of the least soluble P compound in the solid phase controls dissolution and, thus solution P concentration, whereas solution P controls the amount of P sorbed (Syers and Curtin, 1989). In reality, retention of P by soil material is a continuum between precipitation and surface reactions.

11.2.4.1.1 Precipitation–Dissolution

In general, Ca controls these reactions in neutral or calcareous environments, while Al and Fe are the dominant controlling cations in acidic environments. Apatite is the most common primary P mineral ($Ca_{10}(PO_4)_6X_2$, where X is F or OH). Apatite dissolution requires a source of H^+ from soil or biological activity and a sink for Ca and P (Mackay et al., 1986; Smillie et al., 1987):

$$Ca_{10}(PO_4)_2X_2 + 12H^+ = 10Ca^{2+} + 6H_2PO_4^- + 2X^- \qquad (11.3)$$

and occurs during soil development due to weathering (Walker and Syers, 1976). Even though the rate of apatite weathering or dissolution will vary with rainfall and temperature, it is still difficult to predict this first step in the P cycle (Pierzynski, 1991; Pierzynski et al., 2005).

Precipitates in Ca systems occur in the following sequence; monocalcium phosphate [$Ca(H_2PO_4)_2$], dicalcium phosphate dihydrate ($CaHPO_4\ 2H_2O$), octacalcium phosphate

$[Ca_8H_2(PO_4)_6 \cdot 5H_2O]$, and finally hydroxyapatite $[Ca_{10}(PO_4)_6(OH)_2]$ or fluorapatite $[Ca_{10}(PO_4)_6F_2]$, which have low solubilities and should, thus, control soil solution P concentration (Lindsay et al., 1989; Syers and Curtin, 1989).

In Al- and Fe-dominated soils, few well-crystallized precipitates have been observed. Generally, P reacts with Al oxides to form amorphous Al P or organized phases such as sterretite $[Al(OH_2)_3\ HPO_4\ H_2PO_4]$ and with Fe oxides to such precipitates as tinticite $[Fe_6\ (PO_4)_4\ (OH)_6 \cdot 7H_2O)$ or griphite $[Fe_3\ Mn_2\ (PO_4)_2 \cdot 5(OH)_2]$ (Hsu, 1982; Lindsay et al., 1989). Many other amorphous mixed Al–Fe–Si–P compounds have been observed in soils with high P concentrations from phosphatic parent material or large fertilizer or manure applications (Lindsay et al., 1989; Pierzynski et al., 1990b).

11.2.4.1.2 Sorption/Desorption

In most soils, sorption–desorption processes describe P uptake and release by soils that control P availability better than precipitation–dissolution reactions. In this section, the term "sorption" covers surface "adsorption" and subsequent penetration of P into the retaining component or "absorption." Sorption curves or isotherms have been used extensively to describe the relationship between the amount of P sorbed and that remaining in solution (Figure 11.4). For a given solution P concentration, there is a large difference in the amount of P sorbed by the three soil types given as examples. In general, clay content approximates the reactive surface area of a soil responsible for P sorption (Syers et al., 1971; Juo and Fox, 1977; Sharpley et al., 1984a; Hedley et al., 1995). This surface reactivity is a function of the amount and type of hydrous oxides of Al and Fe and reactive Ca components present, other ions (Ca- or Na-dominated), pH of the system, and reaction kinetics.

Even in calcareous soils, hydrous ferric oxides can influence P sorption reactions (Holford and Mattingly, 1975a, 1975b). The types of bonding associated with hydrous oxides and pH dependency have been described in detail by Sample et al. (1980), Uehara and Gillman (1981), and White (1980) (Figure 11.5). Ligand exchange of P at hydrous OH and Fe oxide surfaces results in the formation of monodentate, bidentate, or binuclear complexes (Figure 11.5). As soil solution pH increases, P sorption is decreased by the greater negative charge at the oxide surface and reduced polarization of the Al or Fe–O bond (Figure 11.5).

Soil P sorption has been characterized by parameters calculated from the Langmuir equation:

$$S = \frac{(k S_{max} C)}{1 + kC} \tag{11.4}$$

where

S is sorbed P

C is solution P concentration

S_{max} is the maximum amount of P that can be sorbed

k is an "affinity" constant describing binding energy

Phosphorus sorption maximum is calculated as the reciprocal of the slope of the plot C/S and C and binding energy as the slope/intercept of the same plot (Olsen and Watanabe, 1957; Syers et al., 1973; Graetz and Nair, 2008) (Table 11.3). Equilibrium P concentration is the solution P concentration at which no net sorption or desorption occurs (Figure 11.4 and Table 11.3). These parameters have been widely used to quantify the extent of specific soil reactions and effects of soil types, counter ion and background electrolyte, P source, and soil management on P sorption (Goldberg and Sposito, 1985; Fixen and Grove, 1990). However, the theoretical assumptions of the Langmuir equation were questioned (White, 1980; Barrow, 1989), as sorbed P carries charges that decrease the surface charge and potential of the sorbing surface, leading to large errors in the estimates of S_{max} (Kuo, 1988). The Freundlich equation often fits data better than the Langmuir equation but does not estimate S_{max} (Barrow, 1978).

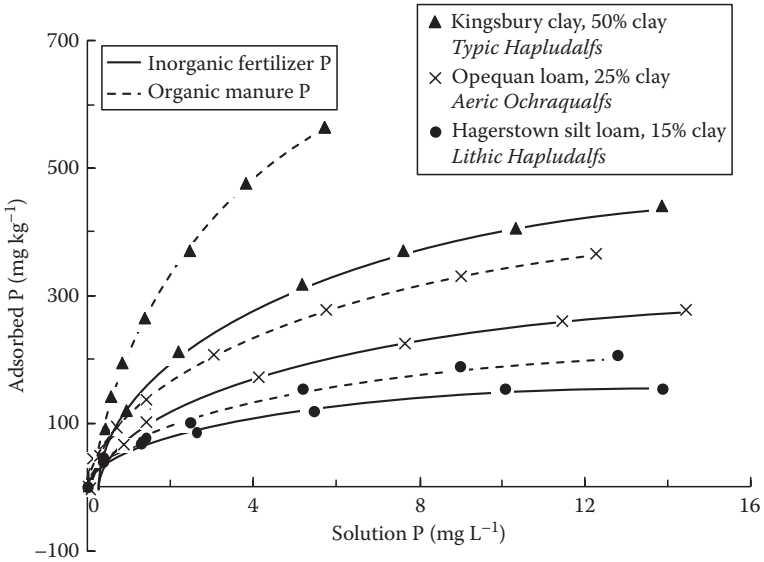

FIGURE 11.4 Phosphorus sorption isotherms as a function of the type of soil and P source.

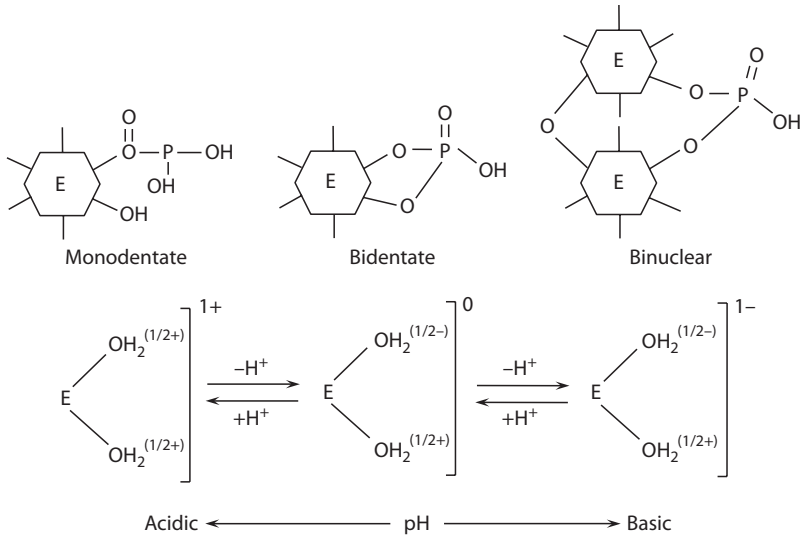

FIGURE 11.5 Types of P bonding associated with hydrous oxides where E is AL or Fe. (Adapted from Fixen, P.E., and J.H. Grove. 1990. Testing soils for phosphorus, p. 141–180. *In* R.L. Westerman (ed.) Soil testing and plant analysis. 3rd edn. SSSA Book Series No. 3. SSSA, Madison, WI.)

TABLE 11.3 Soil P Sorption Properties Calculated from the Langmuir Isotherm as a Function of Soil Type and Source of Added P (Triple Superphosphate and Dairy Manure)

	P Sorption Maxima		Binding Energy		Equilibrium P Concentration	
	Fertilizer	Manure	Fertilizer	Manure	Fertilizer	Manure
Soil Type	(mg kg^{-1})		(L mg^{-1})		(mg L^{-1})	
Hagerstown, sl *Typic Hapludalfs*	172	245	2.17	2.78	0.019	0.044
Kingsbury, c *Aeric Ochraqualfs*	476	909	2.24	3.82	0.069	0.113
Opequon, l *Lithic Hapludalfs*	303	455	1.97	3.09	0.034	0.114

Note: sl, sandy loam; c, clay; l, loam.

Organic anions can compete with P for similar sorption sites on soil surfaces (Yuan, 1980; Hue, 1991; Ohno and Crannell, 1996). However, P sorption can be increased when the addition of organic compounds to amorphous oxides in soil impedes their crystallization and increases specific surfaces (Table 11.3). Also, humic compounds can complex with Fe, Al, and to a lesser extent Ca and sorb P (Levesque and Schnitzer, 1967; Inskeep and Silvertooth, 1988; Frossard et al., 1995).

The release of sorbed P into solution or desorption is not completely reversible. Thus, desorption curves are displaced to the left of the sorption curves. This hysteresis effect is the result of precipitation (Veith and Sposito, 1977), occlusion (Uehara and Gillman, 1981), solid-state diffusion (Barrow, 1983), and bidentate or binuclear bonding with the colloid surface (Hingston et al., 1974).

Several studies have reported that desorption of soil P during a short period of time is a low-activation energy process (Sharpley et al., 1981). The work of Kuo and Lotse (1974) and Evans and Jurinak (1976) reported that the activation energy for P desorption was between 2 and 3 kcal mol^{-1}. The low-activation energies led these researchers to suggest that the desorption of soil P during short reaction times may be limited more by the diffusion of the desorbed P through the stagnant water films present around the soil particles and within the soil aggregates than by the chemical reaction. Although higher-activation energies (20 kcal mol^{-1}) were reported by Barrow and Shaw (1975), they were determined for a longer reaction period (up to 100 days) and represent the transfer of P between desorbable and fixed forms. It has been suggested that there is a continuous range of activation energies for soil P desorption (Posner and Bowden, 1980). During the initial stages of desorption, P held at low-activation energies is desorbed; during the later stages, P held at higher-activation energies is desorbed.

More detailed analysis and review of these chemical processes controlling soil P availability are given by Barrow (1985), Lindsay et al. (1989), Syers and Curtin (1989), Fixen and Grove (1990), Frossard et al. (1995), Condron et al. (2005), and Pierzynski et al. (2005).

11.2.4.2 Biological Processes

Uptake of soluble P by bacteria and fungi, stimulated by the addition of microbial substrates such as litter and crop residues, and release of P as the result of cell lysis or predation (Coleman et al., 1983; Tiessen et al., 1984; Frossard et al., 2000; Jakobsen et al., 2005) are represented in Figure 11.1 as a revolving wheel. This is done deliberately to emphasize the central role of the microbial population in P cycling and availability. For example, if the wheel is stopped or slowed down by lack of C inputs, the supply of P to plants will be limited to the quantity of labile P_i. If the wheel is operating, then solution P is constantly being replenished from labile P_i and P_o forms. Generally, microbial biomass P ranges from 5 to 100 mg kg^{-1} (Srivastava and Singh, 1991; Joergensen et al., 1995; Oberson et al., 1997). As a result, large amounts of P can turnover through microbial biomass annually (He et al., 1997; Oehl et al., 2001; Jakobsen et al., 2005). For example, in a study of P cycling through soil microbial biomass in England, Brookes et al. (1984) measured annual P fluxes of 5 and 23 kg P ha^{-1} $year^{-1}$ in soils under continuous wheat and permanent grass, respectively. Although biomass P flux under continuous wheat was less than P uptake by the crop (20 kg P ha^{-1} $year^{-1}$), annual P flux in the grassland soils was greater than P uptake by the grass (12 kg P ha^{-1} $year^{-1}$).

Within the microbial cell, P exists as a wide variety of compounds, principally RNA (30%–50%), acid soluble P_i and P_o (15%–20%), phospholipids (<10%), and DNA (5%–10%) (Stewart and McKercher, 1982; Condron et al., 2005). If the microbial cell is ruptured or lysed, all these compounds will be released to the soil solution to react with both inorganic and organic soil components to form a host of P_i and P_o compounds of differing solubility or susceptibility to mineralization. The rate of mineralization of P_o forms depends largely on phosphatase activity, which, in turn, can be controlled by solution P concentration (McGill and Cole, 1981; Chen et al., 2002). Stable P_o accumulates in both chemically resistant and aggregate protected forms (Marshall, 1971; Tisdale and Oades, 1982; Condron et al., 2005).

Chemically or physically protected P_o may be slowly mineralized as a by-product of the mineralization of overall soil organic matter or by specific enzyme action in response to the need for P. Therefore, organic matter turnover, as well as solution P_i concentration and the demand for P by microbial and plant components, will be factors controlling the lability of P_o (Richardson, 2000; Turner et al., 2002; Condron et al., 2005). A continuous drain on soil P pools by cultivation and crop removal will rapidly deplete labile P_i and P_o forms and, thereby, reduce available soil P (Hedley et al., 1982; Sharpley and Smith, 1985; Tiessen et al., 1992).

11.2.4.3 Fauna and Flora Processes

The effects of soil fauna (e.g., earthworms and termites) and flora (actinomycetes, bacteria, and fungi) on soil physical, chemical, and biological processes have been extensively studied and reviewed (Reichle, 1977; Lee, 1985; Edwards, 2004). This section outlines the role of the more important of these, earthworms and mycorrhizae, in soil P cycling and their impact on soil P availability.

11.2.4.3.1 Earthworms

Under favorable soil temperature and moisture conditions, earthworms have been found annually to consume 100% of the litter of an evergreen oak forest in Japan (8 Mg ha^{-1} $year^{-1}$ by *A. pheretima*; Sugi and Tanaka, 1978) and mixed deciduous forest in England (3 Mg ha^{-1} $year^{-1}$ by *Lumbricus terrestris*; Satchell, 1967); about 30% of the litter decomposed each year in grass savanna (Lavelle, 1978) and 100% of added cattle manure (17–30 Mg ha^{-1} $year^{-1}$, Guild, 1955). During this consumption, earthworms commonly ingest 100–500 Mg soil ha^{-1} $year^{-1}$ (equivalent to 0.5–3.0 cm of top soil) (Russell, 1973). Consequently, earthworms can have a major influence on soil physical, chemical, and biological properties through incorporation and assimilation of plant litter and associated ingestion of soil material (Lee, 1985; Lavelle, 1988). Egestion as surface and subsurface cast material can rapidly redistribute P in a soil profile, increasing the availability and potential for uptake. Also, earthworm burrowing can allow a greater soil volume to be exploited by plant roots and decrease susceptibility of plants to water stress. Earthworm burrows open to the soil surface increase infiltration rates, enhancing nutrient movement into the profile via macropore flow (Sharpley et al., 1979; Germann et al., 1984; Edwards et al., 1989; Shuster et al., 2003; Dominguez et al., 2004).

The main source of P affected by earthworms is soil organic matter, which includes plant litter in various stages of decomposition, roots, and organic matter in the soil with its complement of microflora and fauna. Ingestion, maceration, and intimate mixing of organic matter with soil increase the rate of humification and mineralization. Although most organic matter undergoes little chemical change during passage through the earthworms' gut, it is finely ground with the increased surface area exposed to microbial activity, facilitating further decomposition. The 5- to 10-fold increase in P content and availability in earthworm casts results from enhanced mineralization of organic P, enrichment of clay-sized particles in casts, and a reduction in P sorption capacity of soil by organic matter blockage (Sharpley and Syers, 1977; Sharpley et al., 1992). Thus, most of the additional P present in casts is held in more physically sorbed than chemisorbed forms, which are readily available to plants.

Both microbial population and activity are increased during passage through the earthworms' gut as a function of the organic matter content of the initial food source (Tiwari, 1979; Gorbenko et al., 1986; Scheu, 1987). Parle (1963) observed that the numbers of bacteria and actinomycetes increased 1000-fold during passage through the gut, and oxygen consumption remained higher in earthworm casts than in soil for 50 days, indicating an increased microbial activity. This enhanced activity is probably responsible for the increased phosphatase activity found in earthworm casts compared to underlying soil (Sharpley and Syers, 1977).

As a result of the incorporation and decomposition of plant material in soil via earthworm activity, soil fertility and

productivity can be improved (Lavelle et al., 1989; Edwards et al., 1995; Katsvairo et al., 2002). For instance, Katsvairo et al. (2002) found that earthworm activity contributed to a 15%–40% increase in corn yields in a soybean (*Glycine max* [L.] Merr.)—wheat (*Triticum aestivum* L.)/clover (*Trifolium pretense* L.)—corn (*Zea mays* L.) rotation on a Kendaia—Lima silt loam in Aurora, New York.

Differences in tillage operation and frequency; amount, type, and quantity of residues left on the soil surface; soil type and climate; and application of manures can influence earthworm populations, species composition, and activity (Pankhurst et al., 1995; Edwards and Bohlen, 1996). For example, several studies have reported an increase in the population and activity of earthworms under reduced compared to conventional tillage practices, concomitant with an increase in food or energy supply (Edwards et al., 1989; Trojan and Linden, 1998; Shipitalo et al., 2000).

The application of manure has been shown to encourage the buildup of earthworm populations in cropped soils to a greater extent than in grass, where there tends to be more decaying organic matter (i.e., food) than in cropped soils (Edwards, 1980; Satchell, 1983). For instance, application of dairy manure (50–400 kg P ha^{-1}) to a rape (*Brassica napus* L.)—sugar beet (*Beta vulgaris* L.)—grass rotation increased the numbers of surface feeding *L. terrestris* by directly increasing their food supply and associated microorganisms (Andersen, 1983). Similarly, the application of dairy manure (20 Mg manure ha^{-1} $year^{-1}$ for 14 year) increased earthworm population, diversity, and activity (mainly *Aporrectodea* and *Lumbricus* genus) in a Le Bras clay loam in Quebec (Estevez et al., 1996).

The potential for earthworm activity to incorporate surface applied manures was demonstrated by Chardon et al. (2007). Disappearance of manure patches deposited by grazing cattle, was partially attributed to earthworm activity, with only 15% of dry matter and 22% of total P in manure patches remaining 234 days after deposition on a permanently grassed sandy soil from Heino, the Netherlands (Chardon et al., 2007). While the manure can remain a long-term source of P to soil leachate, the overall risk of P runoff was reduced as the grassland soil could retain most of the P leached from patches.

11.2.4.3.2 Mycorrhizal Associations

Mycorrhizae are widespread under natural conditions, with vesicular-arbuscular mycorrhizae (VAM) most common in agricultural soils (Smith and Read, 1997; Jakobsen et al., 2005). In fact, VAM are formed by approximately two-thirds of all plants species (Fitter and Moyersoen, 1996) and fungi belonging to the recently established phylum Glomeromycota (Schüssler et al., 2001). Three primary mechanisms by which VAM enhances soil P availability are increased physical exploration of the soil, chemical modification of the rhizosphere, and physiological differences between VAM and plant roots (Read, 2002). For example, extensive hyphal growth of VAM reduced the distance for diffusion of P in soil, thereby increasing uptake. This effect is greater when diffusion limits uptake (Gerdemann, 1968; Facelli and Facelli, 2002). Consequently, a greater response to VAM infection has been exhibited in coarse than in fine rooted plant species (Crush, 1973), in high than in low P sorbing soils (Yost and Fox, 1979), and in soils than in solution culture (Howeler et al., 1982). In addition, the generally smaller diameter of VAM hyphae (2–4 μm) compared to root hairs (710 μm) affords a greater absorptive surface area for hyphae and enables entry of hyphae into soil pores and organic matter that cannot be entered by root hairs (Dodd et al., 2000; Drew et al., 2003).

VAM may chemically modify the rhizosphere through exudation of chelating compounds (Jayachandran et al., 1989; Treeby et al., 1989) or phosphatases (Harley, 1989), which could solubilize poorly soluble soil P. It is clear, however, that VAM utilizes the same sources of P as nonmycorrhizal plants (Mosse et al., 1973; Kucey et al., 1989; Blal et al., 1990), but do so more efficiently.

On a unit weight basis, mycorrhizal plants can rapidly absorb larger amounts of P than nonmycorrhizal plants (Bolan et al., 1987). This difference cannot be accounted for by increased surface area of the hyphae alone; it is, therefore, possible that a greater affinity for P in mycorrhizal plants increased absorption rates. It is also possible that the critical or minimum P concentration, below which there is limited net absorption of P, is lower for mycorrhizal than nonmycorrhizal plants because of an increase in physical contact between hyphae and P, thereby reducing P diffusion distance.

For more detailed information on the role of arbuscular mycorrhizae in influencing soil P availability and plant uptake of P, the reader is directed to the excellent review of Jakobsen et al. (2005).

11.2.5 Optimizing Soil Phosphorus Availability

Critical available soil P concentrations are required to maximize crop yields. These soil concentrations can be optimized by P additions, liming, and cultivation. This section discusses how these factors influence soil P availability; the soil testing and recommendation process that quantifies P additions is discussed in the Chapter 14.

11.2.5.1 Critical Concentrations for Plant Production

Estimates of soil P concentrations, above which little or no crop response to P additions is obtained, vary with the extractant used (Kamprath and Watson, 1980). In many neutral to calcareous soils, 10 mg P kg^{-1} Olsen P was adequate for wheat, alfalfa, and cotton (Olsen et al., 1954). For Bray-1 P, the critical level is about 30 mg P kg^{-1} for Midwestern U.S. soils (Thomas and Peaslee, 1973).

Several additional factors influence the availability of soil P. These include temperature, soil compaction, soil moisture, soil aeration, soil pH, type and amount of clay content, and nutrient (including P) status of soil. When soil temperatures are low during early plant growth, P uptake is reduced. Soil compaction reduces pore space, decreasing the amount of water and oxygen, which, in turn, reduces P uptake. The use of liming materials to increase soil pH, and thereby soil P availability, is an old practice,

which has been adequately reviewed by several authors (Adams, 1984; Kamprath, 1984; McLean and Brown, 1984). Reducing subsoil acidity has not been highly successful due to physical limitations of mixing lime into subsoils. However, surface applications of gypsum with sufficient time for transport into the subsoil have been shown to increase crop yields, increase subsoil Ca, and decrease exchangeable Al (Sumner et al., 1986; Farina and Channon, 1988). Soils with high clay content tend to fix more P than sandy soils with low clay content. Thus, more P needs to be added to raise the soil test level of clay soils than loam and sandy soils. In addition, the presence of ammonium enhances P uptake by creating an acid environment around the root when ammonium ions are absorbed. High concentrations of ammonium-N in the soil with fertilizer P may interfere with and delay normal P fixation reactions, prolonging the availability of fertilizer P (Murphy, 1988).

11.2.5.2 Phosphorus Additions

Optimizing soil P availability through P additions should consider application rate, timing, type, placement, and residual availability (Singh and Lal, 2005). Because of the immobility of P in most soils, the timing of fertilizer P application is not as critical as its placement. Even so, small amounts of placed starter fertilizer for vegetable crops have successfully reduced the need for much larger broadcast applications of P (Costigan, 1988), and a similar strategy (e.g., foliar applications) may be appropriate for other crops. In efforts to minimize P inputs in sustainable or low-input management systems, there has been renewed interest in the estimation and utilization of residual P availability from fertilizer or manure amendments (Pierzynski et al., 1990a; Yerokum and Christenson, 1990; McCollum, 1991; Linquist et al., 1997; Oberson et al., 1999; Tiessen, 2005).

11.2.5.2.1 Rate

The application of P either as mineral fertilizer or animal manure increases available soil P (Table 11.4). In many areas of intensive crop and livestock operations, the application of P at rates greater than crop removal has increased available soil P content above critical concentrations for crop production (Kellogg et al., 2000; Kleinman et al., 2005; Lanyon, 2005; Sharpley et al., 2005). The increase in available soil P ranged from 5 to 31 mg kg^{-1} for every 100 kg ha^{-1} of fertilizer P added (an average 18% increase; Table 11.4). Barber (1979), Rehm et al. (1984), and McCollum (1991) also observed 13%–28% increases in available P following mineral fertilizer P application. These values are similar to proportional increases following application of beef (7–23 mg kg^{-1}; an average 14%), poultry (14–28 mg kg^{-1}; an average 20%), and swine manure (5–20 mg kg^{-1}; an average 11%) (Table 11.4).

In general, annual applications of manure in crop production systems generally results in crop yields comparable to those obtained with commercial fertilizer, especially when applied based on its N content (Sutton et al., 1982; Lucero et al., 1995; Stevenson et al. 1998; Eghball and Power, 1999; Randall et al., 1999; Schmitt et al., 1999; Macoon et al., 2002). However, long-term N-based applications of manure can result in the accumulation of available soil P to levels greater than optimum for crop production (King et al., 1990; Sharpley et al., 1993, 2004; Sims et al., 1998; Mullins et al., 2005).

11.2.5.2.2 Type

Traditional soluble P fertilizers are ordinary superphosphate, triple superphosphate, ammonium polyphosphate, monoammonium phosphate, and diammonium phosphate (Young et al., 1985). The use of slow release P fertilizers, such as partially acidulated rock P (RP), on soils other than those with low pH, Ca, and P content have also been evaluated (Hedley et al., 1989; Muchovej et al., 1989). For example, in soils of neutral pH, it may be possible to apply a heavy initial dressing of finely ground RP and include a rotation of fine rooted legumes to generate a low pH rhizosphere with low Ca concentrations and, thus, increase RP dissolution. Other methods designed to increase acidity in the immediate RP-soil environment, and thereby its dissolution, include addition of elemental S (Muchovej et al., 1989), NH_4^+ fertilizers, or organic matter such as animal manure and crop residues (Hedley et al., 1989).

Animal manure itself is a valuable resource of P for crop production. The availability of P in manure in some soils may differ from fertilizer P (Table 11.3; Figure 11.4; Hue, 1991; Frossard et al., 1995). As a major proportion of P in manure can be organic (25%–50%), biological processes in soil will play a greater role in determining P availability than for fertilizer P, when applied at equivalent rates of P. In as much, the slower release of P from manure may make it a longer-term source of P to crops than more readily soluble fertilizer P.

Adding manure can cause an increase in soil pH (Kingery et al., 1994; Iyamuremye et al., 1996; Eghball, 2002), due to input of large amounts of Ca (up to 60 g Ca kg $manure^{-1}$) and the buffering effects of added bicarbonates and organic acids with carboxyl and phenolic hydroxyl groups (Sharpley and Moyer, 2000; Whalen et al., 2000). This suggests that not only the amounts but also form, solubility, and relative availability of soil P for crop uptake and release to overland flow can change with manure application (Wang et al., 1995). In fact, Sharpley et al. (2004) found that the long-term application (10–25 years) of dairy, poultry, or swine manure to 20 sites in New York, Oklahoma, and Pennsylvania resulted in an average increase in soil pH from 5.9 to 6.6, exchangeable Ca from 0.9 to 6.2 g kg^{-1}, organic C from 15.7 to 32.6 g kg^{-1}, and total P from 407 to 2480 mg kg^{-1}, between untreated and treated sites. What was more important to soil P availability was that as Mehlich-3 P increased (22–662 mg kg^{-1}), the proportion that was water soluble (14%–3%) declined as exchangeable Ca increased ($R^2 = 0.81$). Ion-activity products suggested that addition of manure to soil shifts P from Al– and Fe– to Ca–P reaction products, accounting for the relatively greater Mehlcih-3 P but lower water extractability of soil P (Sharpley et al., 2004). This has important implications for agronomic and environmental soil P testing, where acid-based extractants, such as Mehlich-3 and Bray may dissolve Ca–P complexes in manured soils that may not accurately reflect plant availability or potential for release to runoff. For instance, this may explain

TABLE 11.4 Available Soil P of Soil Treated with Fertilizer or Manure for Several Years and Untreated Soil in the U.S. and U.K. Studies

Soil	Crop	Added P (kg ha^{-1} Year^{-1})	Time (Year)	Available Soil P			Reference and Location
				Method	Untreated	Treated	
				(mg kg^{-1})			
Fertilizer							
Portsmouth, fsl *Typic Umbraquult*	Mixed veg.	20	9	Mehlich I	18	73	Cox et al. (1981); North Carolina and Rothamsted
Batcombe, cl *Typic Haploborolls*	Mixed veg.	27	19	Olsen	16	44	
Richfield, scl	Mixed veg.	20	14	Bray 1	12	54	Hooker et al. (1983); Kansas
Aridic Argiustolls		40	14	Bray 1	12	56	
Pullman, cl *Torrertic Paleustolls*	Sorghum	56	8	Bray 1	15	76	Sharpley et al. (1984b); Texas
Keith, sil *Aridic Argiustolls*	Wheat	11	6	Bray 1	22	31	McCallister et al. (1987); Nebraska
Rosebud, sil	Wheat	33	6	Bray 1	24	47	
Aridic Argiustolls		11	6		10	28	
		33	6		10	48	
Beef manure							
Lethbridge, cl	Barley	160	11	Bray 1	22	424	Chang et al. (1991); Alberta
Typic Haploborolls		320	11		22	736	
		480	11		22	893	
Pullman, cl	Sorghum	90	8	Bray 1	15	63	Sharpley et al. (1984b); Texas
Torrertic Paleustolls		273	8		15	230	
Poultry litter							
Cahaba, vfsl *Typic Hapludults*	Grass	130	12	Bray 1	5	216	Sharpley et al. (1993); Oklahoma
Ruston, fsl *Typic Paleudults*	Grass	100	12	Bray 1	12	342	
Stigler, sl *Aquic Paleudalfs*	Grass	35	35	Bray 1	14	239	
Swine manure							
Norfolk, l	Grass	109	11	Mehlich I	80	235	King et al. (1990); North Carolina
Typic Kandiudults		218	11		80	310	
		437	11		80	450	
Captina, sl *Typic Fragiudults*	Grass	101	9	Bray 1	5	121	Sharpley et al. (1991); Oklahoma
Sallisaw, l *Typic Paleudalfs*	Grass	81	15	Bray 1	6	147	
Stigler, sl *Aquic Paleudalfs*	Wheat	37	9	Bray 1	15	82	
Cecil, sl	Grass	160	3	Mehlich I	19	45	Reddy et al. (1980); North Carolina
Typic Kanhapludults		320	3		19	100	

Note: vfsl, very fine sandy loam; fsl, fine sandy loam; sl, sandy loam; sil, silt loam; l, loam; scl, silty clay loam; cl, clay loam; c, clay.

the plateau in the relationship between Mehlich-3 P and runoff dissolved P observed by Torbert et al. (2002). Thus, at high soils P levels Mehclih-3 P is likely extracting some P that may not be immediately released from manured surface soil to runoff.

11.2.5.2.3 Placement

Due to the general immobility of P in the soil profile, fertilizer placement is generally more critical for P than N. Depending on soil and environmental factors, band applications of P may or may not be better than broadcast incorporated applications of P. The effect of P application also varies with soil type. For six soils having a 100-fold variation in P sorptivity, Holford (1989) found that fertilizer P effectiveness, as measured by yield response in the first crop (wheat), residual effect in the second crop (clover), or cumulative recovery of applied P, was consistently greater for shallow banding at 5 cm depth compared to banding at 15 cm or broadcast applications. The almost equal effect obtained by mixing P throughout the soil, regardless of P sorptivity, suggested that the positional availability of P in the root zone is important in maximizing fertilizer effectiveness (Holford, 1989) in addition to reducing P sorption.

Positional availability is also influenced by crop type. In order for banding or restricted fertilizer placement to increase potential root extraction of P, the rate of P absorption and growth of roots in fertilized soil must increase to compensate for roots in unfertilized soil. Increased root growth and P uptake in the P-fertilized volume of soil compared to unfertilized soil has been observed for corn (Anghinoni and Barber, 1980), soybeans (Borkert and Barber, 1985), and wheat (Yao and Barber, 1986). In contrast, several studies have shown that flax does not respond to banded fertilizer due to an inability of its root system to expand and proliferate into and efficiently absorb P from high concentrations in the fertilized zone (Soper and Kalra, 1969; Strong and Soper, 1974). In the case of flax, increased P uptake and yield response was obtained when fertilizer P was placed 2–5 cm directly below the seed, ensuring adequate P levels during early growth (Bailey and Grant, 1989).

Field variability in soil properties, crop-yield potential, and topographic differences can affect site-specific requirements of P. For example, mixing a few fertile soil subsamples with any number of subsamples with marginal nutrient availability can produce misleading analytical results. An example from Nebraska, where scientists extensively sampled a 58 ha cornfield, illustrates this situation (Hergert et al., 1994; Peterson et al., 1994). More than 2000 cores collected from a 58 ha cornfield showed that about 75% of the field would likely respond to P fertilization. Yet, composited annual soil samples indicated a need for little, if any, P fertilizer. Further investigation disclosed the existence of an old farmstead that included a swine feeding operation from 20 years earlier and another area where sheep had been fed in confinement more than 70 years ago.

Integration of the spatial variability of soil properties into fertilizer management and placement decisions will receive greater attention as agronomic response models are developed that incorporate the information now readily available through precision agriculture technology. Such technology, coupled with soil and nutrient management information, will facilitate the correct rate and method of N and P application to meet crop needs.

11.2.5.2.4 Residual Availability

Halvorson and Black (1985) showed that soil test P levels were increased above the initial available P level for more than 16 years, by a one-time P application on a Williams loam (*Typic Argiborolls*) in Montana (Figure 11.6). After the initial increase, available P levels declined for about 12 years and then stabilized at a higher available level than was initially present, thus establishing what appears to be a new equilibrium level of available P. Fixen (1986) reported similar changes in available P levels with time. Crop yields, reported by Halvorson and Black (1985), were also improved by the residual P fertilizer for a period of 16 years (Figure 11.6).

The rate of decline in soil P in high P soils when no further P is added varies with soil type and management (Table 11.5). The rate of decline in available soil P ranged from 0.1 to 30 mg kg^{-1} $year^{-1}$. McCollum (1991) estimated that without further P, 16–18 years of corn (*Z. mays* L.) or soybean (*G. max* (L.) Merr.) production would be needed to deplete soil P (Mehlich-3 P) in a Portsmouth fine sandy loam (*Typic Umbraquults*) from 100 mg P kg^{-1} to the agronomic threshold level of 20 mg P kg^{-1}. Several authors have found the rate of decrease in available soil P with depletion by cropping when no P is added is inversely related to the soil's P buffering capacity (Holford, 1982; Aquino and Hanson, 1984; Dodd and Mallarino, 2005) or P sorption saturation (available soil P/P sorption maximum; Sharpley, 1996).

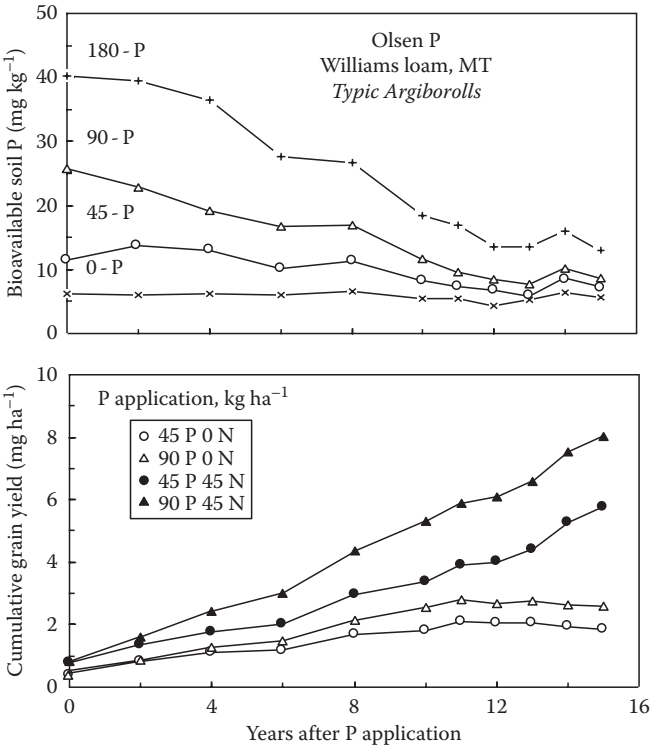

FIGURE 11.6 Changes in bioavailable soil P (Olsen P) and cumulative wheat yields following a single application of fertilizer P. (Data adapted from Halvorson, A.D., and A.L. Black. 1985. Long-term dryland crop responses to residual phosphorus fertilizer. Soil Sci. Soc. Am. J. 49:928–933.)

TABLE 11.5 The Decrease in Available Soil P after P Application Was Stopped in Several North American P Studies

Soil	Crop	Time (Year)	Method	Available Soil P: Initial (mg kg^{-1})	Available Soil P: Final (mg kg^{-1})	Decline (mg kg^{-1} Year^{-1})	Reference and Location
Thurlow, l	Small grains	9	Olsen	13	4	1.0	Campbell (1965); Montana
Ustollic Haplargids		9		20	4	1.8	
		9		60	6	6.0	
Georgeville, scl	Small grains	7	Mehlich I	3	1	0.1	Cox et al. (1981); North Carolina and Saskatchewan
Typic Hapludult		7		7	2	0.6	
Haverhill, c	Wheat—fallow	14	Olsen	40	25	1.1	
Typic Epiaquolls l		14		74	33	2.9	
		14		134	69	4.6	
Portsmouth, fsl	Small grains	8	Mehlich I	23	18	0.6	
Typic Umbraqualts		9		54	26	3.1	
Sceptre, c	Wheat—fallow	8	Olsen	45	18	3.4	
Typic Haploborolls		8		67	18	6.1	
		8		147	40	13.4	
Williams, l	Wheat—barley	16	Olsen	26	8	1.1	Halvorson and Black (1985); Montana
Typic Argiborolls		16		45	14	1.9	
Richfield, scl	Corn	8	Bray 1	12	8	0.5	Hooker et al. (1983); Kansas
Aridic Argiustolls		8		22	14	1.0	
Carroll, cl	Wheat—flax	8	Olsen	71	10	7.6	Spratt et al. (1980); Manitoba
Typic Haploborolls		8		135	23	14.0	
		8		222	50	21.5	
Waskada, l	Wheat—flax	8	Olsen	48	9	4.9	
Typic Haploborolls		8		88	23	8.1	
		8		200	49	18.9	
Waskada, cl	Wheat—flax	8	Bray 1	140	50	11.3	Wagner et al. (1986); Manitoba
Typic Haploborolls		8		320	80	30.0	

Note: fsl, fine sandy loam; l, loam; scl, silty clay loam; cl, clay loam; c, clay.

11.2.5.3 Land Management

11.2.5.3.1 Cultivation

Cultivation and associated fertilizer applications can influence the amount of soil P_i and P_o and should be considered in optimizing soil P availability. Thompson et al. (1954) measured a decrease in P_i and P_o content of 25 surface (0–15 cm) soils from Iowa, Texas, and Colorado, with cultivation. Similarly, Adepetu and Corey (1976) reported that 25% of the P_o content of the surface of a Nigerian soil was mineralized during the first two cropping periods following cultivation. In fact, P_i changes little with crop removal and no fertilizer P application, but available P declines gradually. The net loss from the system through removal in the harvested crop is primarily accounted for by a decrease in P_o. For example, 60 years (1913–1973) of cotton growth on the Mississippi Delta soil, Dundee silt loam (Typic Endoaqualfs), with no reported P added, resulted in no appreciable effect on P_i (Sharpley and Smith, 1983). However, the P_o content of cultivated (93 mg kg^{-1}) compared to virgin analogue (223 mg kg^{-1}) surface soil (0–15 cm) decreased. Mineralization of P_o slowly replenished the P_i pool, which resulted in a 50% reduction in Bray-1 available P. Where cultivation involved P application, P_i and P_o increased 130% and 227%, respectively, while Bray-1 available P increased 84% and P sorption capacity decreased 33% on an average for 8 U.S. agricultural soils (Sharpley and Smith, 1983).

11.2.5.3.2 Remediation of High P Soils

Large amounts of coal combustion by-products are produced annually by power plants in compliance with clean air legislation (U.S. Environmental Protection Agency, 1988). These by-products can be used safely to increase soil pH and reduce subsoil acidity (Stout and Priddy, 1996; Stout et al., 1999; Callahan et al., 2002). Recent research also suggests that two of these by-products—fluidized bed combustion fly ash and flue gas desulfurization gypsum—can greatly reduce water-soluble P levels in soils and surface runoff without appreciably reducing the plant-available P and plant growth; moreover, heavy metals and arsenic in plants or runoff water are not increased (Stout et al., 1998, 2000).

The use of these amendments on critical areas of a watershed has the potential to make large albeit short-term reductions in P loss (Stout et al., 1999).

11.2.6 Water Quality Implications of Soil Phosphorus Availability

Many studies have reported that the loss of dissolved P in surface runoff is dependent on the available P content of surface soil as measured by soil P test extractants (Sharpley et al., 1996; Pote et al., 1999b; Pierson et al., 2001; Torbert et al., 2002; Andraski and Bundy, 2003; Daverede et al., 2003). For instance, runoff P—soil P relationships were developed within a 40 ha watershed (FD-36) in south-central Pennsylvania (Northumberland Co.), where there was a wide range in soil test P concentration as Mehlich-3 P (20–600 mg L^{-1}) (McDowell and Sharpley, 2001; Sharpley et al., 2001). As Mehlich-3 soil P increased, so did the concentration of dissolved P in surface runoff from 2 m^2 plots subjected to a 30 min rainfall of 7 cm h^{-1} (Figure 11.7). Similarly, the concentration of P in subsurface flow is also related to surface soil P (Figure 11.7). Lysimeters of 30 cm depth were taken from the same Pennsylvania watershed and subjected to simulated rainfall (1 cm h^{-1} for 30 min). The concentration of dissolved P in drainage from the lysimeter increased (0.07–2.02 mg L^{-1}) as the Mehlich-3 P concentration of surface soil increased (Figure 11.7; McDowell and Sharpley, 2001; Sharpley et al., 2001). The dependence of leachate P on surface soil P is evidence of the importance of P transport in preferential flow pathways such as macropores, earthworm holes, and old root channels.

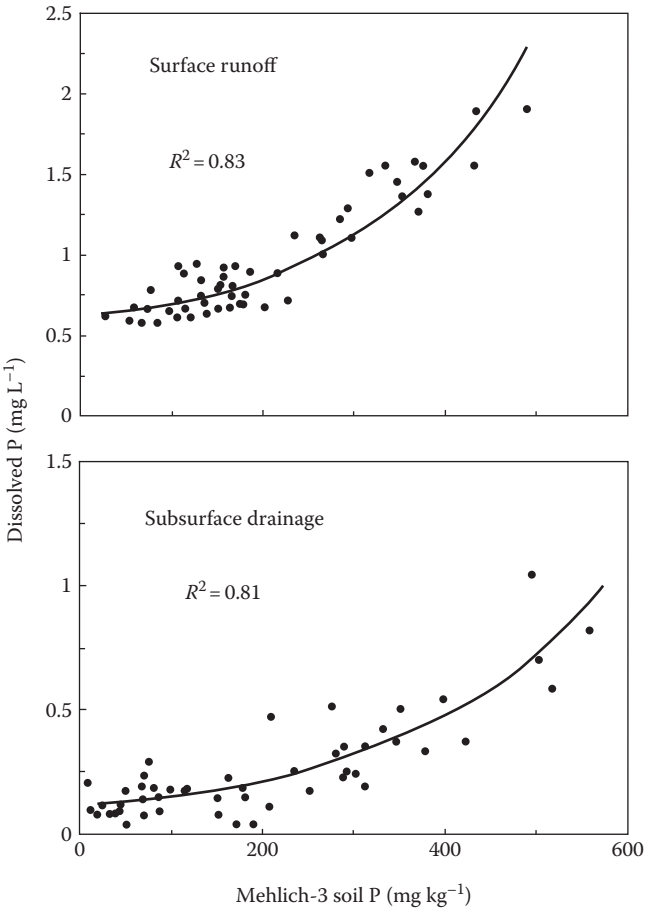

FIGURE 11.7 Relationship between the concentration of dissolved P in surface runoff from 2 m^2 plots and subsurface drainage from 30 cm deep lysimeters and surface soil (0–5 cm depth) Mehlich-3 extractable P concentration from a central PA watershed.

Vadas et al. (2005) conducted a detailed review of the large amount of research published since the late 1990s on the relationship between soil P availability and runoff dissolved P (Table 11.6). Clearly, there was a range in the extraction coefficient representing the slope of the soil P—runoff P relationship or in more simple terms, the extractability of soil P by runoff water. Significant differences among extraction coefficients were not related to any one soil physical, chemical, or management factor (Vadas et al., 2005). The most likely factor influencing soil P extractability was site hydrology, such that a greater proportion of applied rainfall as runoff translated into more P being desorbed from the surface soil and transported in runoff (Vadas et al., 2005). When these studies were combined to include runoff from soil boxes and field plots that were tilled, notilled, cropped, and grassed, a single extraction coefficient of 2.0 related Mehlich-3 soil P (mg kg^{-1}) to runoff dissolved P (μg L^{-1}).

This information supports the use of soil test P as a measure of soil P availability in estimating the potential for dissolved P enrichment of runoff, as used in nonpoint source models and more recently in estimating the environmental implications of soil P on runoff P, in relation to impairment of surface waters. Thus, as we move from agronomic to environmental concerns with P, where continued applications of P usually as manure, have led to increased available soil P above optimum levels for crop production, soil P testing is being used to indicate when P enrichment of runoff may become unacceptable. Because of this, a common approach has been to use agronomic soil P standards, following the rationale that soil P in excess of crop requirements is vulnerable to removal by surface runoff or leaching. As agronomic standards already exist for soil test P, this approach required little investment in research and development and can be readily implemented. However, we must be careful how we interpret soil test results for environmental purposes (Figure 11.8).

Interpretations given on soil test reports (i.e., low, medium, optimum, high, etc.) are based on expected crop yield response to P and not on soil P release to surface or subsurface runoff (Sharpley et al., 1994). Some have tried to simply extend crop response levels and say that a soil test that is above the level where a crop response is expected is in excess of crop needs and therefore is potentially polluting (Figure 11.8). However, two factors are of critical importance to the debate on how to use soil test P in environmental risk assessment. First, the gap between crop and environmental soil P thresholds reflects the difference in soil P removed by an acid or base extractant (i.e., Mehlich, Bray, Olsen agronomic tests) and by less invasive water (i.e., simulating extraction of soil P by runoff water), which is soil specific. Secondly, soil P is only one of several factors influencing the

TABLE 11.6 Extraction Coefficients Relating Soil P Availability (mg kg^{-1}) to Runoff Dissolved P (DP; μg L^{-1})

Reference	Location	Land Use	Soil	Number of Observations	Runoff DP	Extraction Coefficient	
						Bray-1	Mehlich-3
Aase et al. (2001)	Indiana	Tilled plots	sl	48	0–0.4	—	—
Andraski and Bundy (2003)	Wisconsin	Cropped plots	sl, cl	126	0–1.0	2.0–13.0	1.3–3.0
Andraski et al. (2003)	Wisconsin	Cropped plots	sl	127	0–0.3	1.9–2.6	1.7
Cox and Hendricks (2000)	North Carolina	Cropped plots	cl, ls	20	0–2.0	—	1.4–3.9
Daverede et al. (2003)	Illinois	Cropped plots	scl	64	0–1.0	0.6–0.8	—
Fang et al. (2002)	Minnesota	Soil boxes	scl, cl, c	10	0–1.0	9.8	5.8
McDowell and Sharpley (2001)	Pennsylvania	Soil boxes, pasture, tilled plots	sl	88	0–1.0	—	1.7–1.9
Pote et al. (1996)	Arkansas	Fescue plots	sl	54	0.2–1.6	2.2	2.6
Pote et al. (1999a)	Arkansas	Fescue plots	sl, sal	36	0–1.2	2.7–4.3	1.6–3.6
Pote et al. (1999b)	Arkansas	Fescue plots	sl	36	0–1.4	—	2.2–2.8
Schroeder et al. (2004)	Georgia	Pasture plots	sal	54	0–1.1	—	1.7–2.0
Sharpley et al. (2001)	Pennsylvania	Pasture tilled plots	sl	—	—	—	2.1
Torbert et al. (2002)	Texas	Bermudagrass plots	sal, cl, c	72	0–1.6	—	0.4–7.0
Turner et al. (2004)	Idaho	Tilled plots	sl, fsl	50	0–0.7	—	1.2–2.8
Weld et al. (2001)	Pennsylvania	Soil boxes	sl	—	—	—	1.5–1.7

Source: Adapted from Vadas, P.A., P.J.A. Kleinman, and A.N. Sharpley. 2005. Relating soil phosphorus to dissolved phosphorus in runoff: A single extraction coefficient for water quality modeling. J. Environ. Qual. 34:572–580.

Note: fsl, fine sandy loam; fas, sandy loam; sl, silt loam; scl, silty clay loam; cl, clay loam; c, clay.

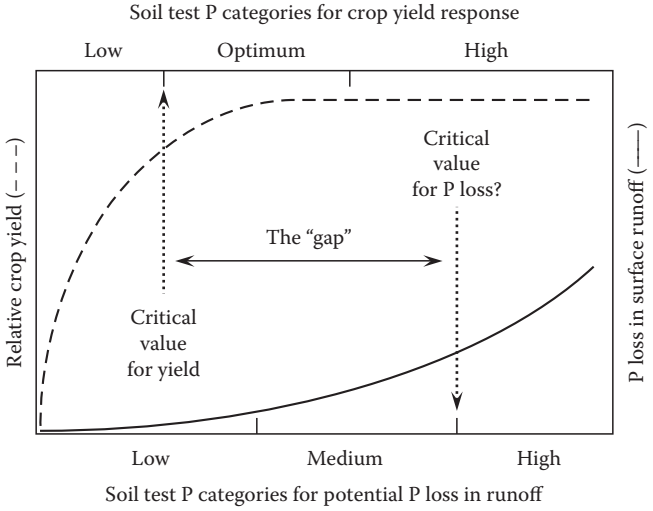

FIGURE 11.8 As soil P increases, so does crop yield and the potential for P loss in surface runoff. The interval between the critical soil P value for yield and runoff P will be important for P management.

potential for P loss; therefore, soil test P should not be used as the sole criteria on which to base P management planning.

11.2.7 Conclusions

The amount and availability of soil P is determined by physical, chemical, and biological processes, which are often managed in attempts to increase or optimize crop uptake of P and yields. In many areas, P cycles have been fragmented by the specialization of agricultural production systems in specific regions. For instance, mineral fertilizer P is imported to areas of crop production from continental United States and overseas deposits, which have been treated to varying degree to increase P solubility. The harvested grain is used to meet human demands, for animal feed, and more recently as biofuel feedstock. In each case, major population areas, confined animal operations, and biorefineries are geographically removed from areas of crop production. For example, most of the corn produced in the Midwest is used as feed in eastern U.S. states. As a result, P is moving from areas where ore deposits are mined, through crop producing regions, and is accumulating in areas of confined animal operations.

Future management of soil P availability must address the impacts that this specialization of agricultural systems is having on regional P requirements and production on a national scale. At the farm scale, however, efforts should continue to find ways of enhancing the efficient use of P, through soil testing, appropriate rates of P application, and utilization of manure sources of P in an increasing number of agricultural production systems. If these goals are not met, soil P availability may become an environmental rather than fertility issue in more areas.

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11.3 Bioavailability of Soil Potassium

Donald L. Sparks

11.3.1 Introduction

The role of K in soils is prodigious. Of the many plant nutrient–soil mineral relationships, those involving K are of major, if not prime, significance (Sparks and Huang, 1985; Sparks, 1999).

Since the middle of the seventeenth century, when J.R. Glauker in the Netherlands first proposed that saltpeter (KNO_3) was the principle of vegetation, K has been recognized as being beneficial to plant growth (Russell, 1961). Glauker obtained large increases in plant growth from the addition of saltpeter to the soil that was derived from the leaching of coral soils. The essentiality of K to plant growth has been known since the work of von Liebig.

Of the major nutrient elements, K is usually the most abundant in soils (Reitemeier, 1951). Igneous rocks of the Earth's crust have higher K contents than sedimentary rocks. Of the igneous rocks, granites and syenites contain 46–54, basalts 7, and peridotites 2.0 g K kg^{-1}. Among the sedimentary rocks, clayey shales contain 30, whereas limestones have an average of only 6 g K kg^{-1} (Malavolta, 1985).

Mineral soils generally range between 0.04% and 3% K. Total K contents in soils range between 3000 and 100,000 kg ha^{-1} in the upper 0.2 m of the soil profile. Of this total K content, 98% is bound in the mineral form, whereas 2% is in soil solution and exchangeable phases (Schroeder, 1979; Bertsch and Thomas, 1985).

Potassium, among mineral cations required by plants, is the largest in nonhydrated size ($r = 0.133$ nm) and the number of oxygen atoms surrounding it in mineral structures is high (8 or 12), which suggests that the strength of each K–O bond is relatively weak (Sparks and Huang, 1985). Potassium has a polarizability equal to 0.088 nm^3, which is higher than for Ca^{2+}, Li^+, Mg^{2+}, and Na^+ but lower than for Ba^{2+}, Cs^+, NH_4^+, and Rb^+ ions (Rich, 1968, 1972; Sparks and Huang, 1985). Ions with higher polarizability are preferred in ion-exchange reactions. Potassium has a hydration energy of 142.5 kJ g^{-1} ion^{-1}, which indicates little ability to cause soil swelling (Helfferich, 1962).

11.3.2 Forms of Soil Potassium

Soil K exists in four forms in soils: solution, exchangeable, fixed or nonexchangeable, and structural or mineral (Figure 11.9). Quantities of exchangeable, nonexchangeable, and total K in the surface layer (0–20 cm) of a variety of soils are shown in Table 11.7. Exchangeable K and nonexchangeable K levels comprise a small portion of the total K. The bulk of total soil K is in the mineral fraction (Sparks and Huang, 1985). There are equilibrium and kinetic reactions between the four forms of soil K that affect the level of soil solution K at any particular time and, thus, the amount of readily available K for plants. The forms of soil K in the order of their availability to plants and microbes are solution > exchangeable > fixed (nonexchangeable) > mineral (Sparks and Huang, 1985; Sparks, 1987, 1999).

11.3.2.1 Solution K

Soil solution K is the form of K that is directly taken up by plants and microbes and also is the form most subject to leaching in soils. Levels of soil solution K are generally low, unless recent

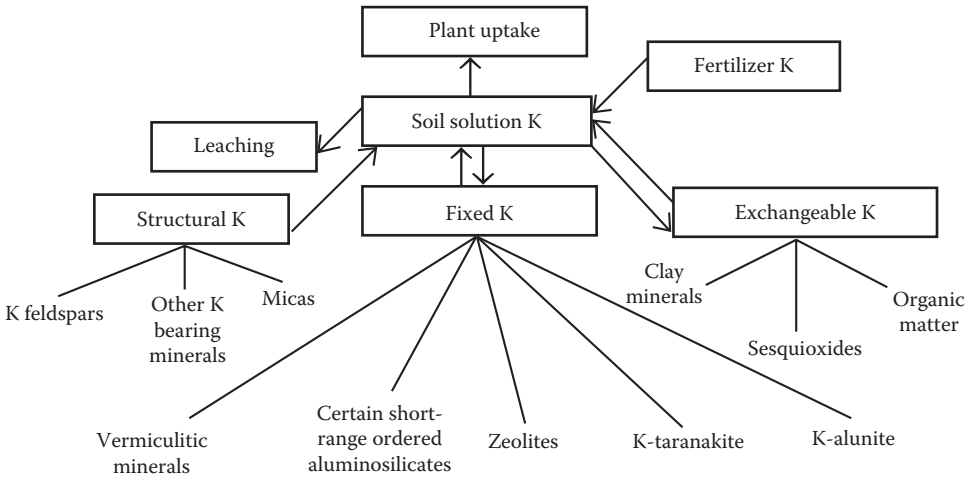

FIGURE 11.9 Interrelationships of various forms of soil K. (From Sparks, D.L., and P.M. Huang. 1985. Physical chemistry of soil potassium, p. 201–276. *In* R.D. Munson (ed.) Potassium in agriculture. ASA, Madison, WI. With permission of American Society of Agronomy.)

TABLE 11.7 Potassium Status of Selected Soils[a]

Origin of Soil	Exchangeable K	Nonexchangeable K	Total K	Source
	($cmol_c\ kg^{-1}$)			
Alfisols				
Nebraska, USA	0.40	—	—	Soil Survey Staff (1975)
West Africa	0.46	—	3.07	Juo (1981)
Inceptisols				
California, USA	0.40	—	—	Soil Survey Staff (1975)
Maryland, USA	0.20	—	—	Soil Survey Staff (1975)
Mollisols				
Iowa, USA	0.27	—	—	Survey Staff (1975)
Nebraska, USA	0.40	—	—	Survey Staff (1975)
Ultisols				
Delaware, USA	0.33	0.49	22.5	Parker et al. (1989a)
Florida, USA	0.14	0.25	2.71	Yuan et al. (1976)
Virginia, USA	0.11	0.17	6.5	Sparks et al. (1980)
West Africa	0.24	—	8.06	Juo (1981)

[a] Data are for surface soils (0–20 cm depth).

amendments of K have been made to the soil. The quantity of K in the soil solution varies from 2 to 5 mg K L^{-1} for normal agricultural soils of humid regions and is an order of magnitude higher in arid region soils (Haby et al., 1990). Levels of solution K are affected by the equilibrium and kinetic reactions that occur between the forms of soil K, the soil moisture content, and the concentrations of bivalent cations in solution and on the exchanger phase (Sparks and Huang, 1985; Sparks, 1999).

11.3.2.2 Exchangeable K

Exchangeable K is the portion of the soil K that is electrostatically bound as an outer-sphere complex to the surfaces of clay minerals and humic substances. It is readily exchanged with other cations and also is readily available to plants.

11.3.2.3 Nonexchangeable K

Nonexchangeable or fixed K differs from mineral K in that it is not bonded within the crystal structures of soil mineral particles. It is held between adjacent tetrahedral layers of dioctahedral and trioctahedral micas, vermiculites, and intergrade clay minerals such as chloritized vermiculite (Rich, 1972; Sparks and Huang, 1985; Sparks, 1987). Potassium becomes fixed because the binding forces between K and the clay surfaces are greater than the hydration forces between individual K^+ ions. This results in a partial collapse of the crystal structures and the K^+ ions are physically trapped to varying degrees, making K release a slow, diffusion controlled process (Sparks, 1987). Nonexchangeable K also can be found in wedge zones of weathered micas and vermiculites (Rich, 1964). Only ions with a size similar to K^+, such as NH_4^+ and H_3O^+, can exchange K from wedge zones (Chapter 21 of *Handbook of Soil Sciences: Properties and Processes*). Large hydrated cations, such as Ca^{2+} and Mg^{2+}, cannot fit into the wedge zones. Release of nonexchangeable K to the exchangeable form occurs when levels of exchangeable and soil solution K are decreased by crop removal and/or leaching and perhaps by large increases in microbial activity (Sparks, 1980).

Nonexchangeable K is moderately to sparingly available to plants (Mengel, 1985; Sparks and Huang, 1985; Sparks, 1987). Mortland et al. (1956) showed that biotite could be altered to vermiculite by plant removal of K. Schroeder and Dummler (1966) showed that the nonexchangeable K associated with some German soil illites was an important source of K to crops. The ability of plants to take up nonexchangeable K appears to be related to the plant species. Steffens and Mengel (1979) found that ryegrass (*Lolium perenne*) could take up nonexchangeable K longer without yield reductions, while red clover (*Trifolium pratense*) could not. This was attributed to the ryegrass having longer root length, which would allow it to grow at a relatively low K concentration. A similar concentration would result in a K deficiency in red clover. It may be that the difference in root mass, root length, and root morphology between monocots and dicots explains why monocots feed better from nonexchangeable K than dicots (Mengel, 1985).

11.3.2.4 Mineral K

As noted earlier, most of the total K in soils is in the mineral form, mainly as K-bearing primary minerals such as muscovite, biotite, and feldspars. For example, in some Delaware soils, Sadusky et al. (1987) found that mineral K comprised about 98% of the total K (Table 11.8). Most of the mineral K was present as K feldspars in the sand fractions.

Common soil K-bearing minerals, in the order of availability of their K to plants, are biotite, muscovite, orthoclase, and microcline (Huang et al., 1968; Sparks, 1987). Mineral K is generally assumed to be only slowly available to plants; however, the availability is dependent on the level of K in the other forms, and the degree of weathering of the feldspars and micas constituting the mineral K fraction (Sparks and Huang, 1985; Sparks, 1987).

TABLE 11.8 Potassium Status of Delaware Soils and Sand Fractions

		Soils				Sand Fraction	
Horizon	Depth (cm)	$CaCl_2$ Extractable	HNO_3 Extractable	Mineral K[a]	Total K	Total K[b]	K Feldspars[c] Frequency (%)
		($cmol_c\ kg^{-1}$)					
Kenansville loamy sand							
Ap	0–23	0.25	0.42	35.02	35.69	30.88	9.5
Bt2	85–118	0.25	0.49	45.30	46.04	33.86	12.0
Rumford loamy sand							
Ap	0–25	0.33	0.49	21.67	22.51	18.62	6.7
BC	89–109	0.21	0.54	23.39	23.96	16.76	8.2
Sassafras fine loamy sand							
Ap	0–20	0.35	0.56	43.54	44.45	28.95	16.0
Cl	84–99	0.13	0.36	45.99	46.68	36.69	24.0

Source: Sadusky, M.C., D.L. Sparks, M.R. Noll, and G.J. Hendricks. 1987. Kinetics and mechanisms of potassium release from sandy soils. Soil Sci. Soc. Am. J. 51:1460–1465. With permission of the Soil Science Society of America.

[a] Mineral K = [(total K) − ($CaCl_2$ ext. K + HNO_3 ext. K)].

[b] These data represent the amount of total K in the sand based on a whole soil basis.

[c] Determined through petrographic analyses of the whole sand fractions and represents the percentage of total point counts in a given sample that were K feldspars. The remaining minerals in the sand fraction were quartz, plagioclase, and opaques.

Sadusky et al. (1987) and Parker et al. (1989a, 1989b) have found that a substantial amount of K is released from the sand fractions of Delaware soils that are high in K feldspars. This finding, along with the large quantities of mineral K in these and other Atlantic Coastal Plain soils, could help in explaining the often observed lack of crop response to K amendments on these soils (Liebhardt et al., 1976; Yuan et al., 1976; Sparks et al., 1980; Woodruff and Parks, 1980; Parker et al., 1989a).

11.3.3 Factors Affecting Potassium Availability

11.3.3.1 Solution-Exchangeable K Dynamics

The rate and direction of reactions between solution and exchangeable forms of K determine whether applied K will be leached into lower horizons, taken up by plants, converted into unavailable forms, or released into available forms.

The reaction rate between soil solution and exchangeable phases of K is strongly dependent on the type of clay minerals present (Sivasubramaniam and Talibudeen, 1972; Sparks et al., 1980; Sparks and Jardine, 1981, 1984; Jardine and Sparks, 1984) and the method employed to measure kinetics of K exchange (Sparks, 1989, 1995; Amacher, 1991; Sparks et al., 1996). Vermiculite, montmorillonite, kaolinite, and hydrous mica vary drastically in their ionic preferences, ion binding affinities, and types of ion-exchange reactions. Such fundamental differences in these clay minerals account for the varying kinetics of K exchange.

Kinetics of K exchange on kaolinite and montmorillonite are usually quite rapid (Malcolm and Kennedy, 1969; Sparks and Jardine, 1984; Sparks, 1995, 2002). An illustration of this is shown in Figure 11.10. In the case of kaolin clays, the tetrahedral layers of adjacent clay layers are held tightly by H bonds; thus, only planar external surface and edge sites

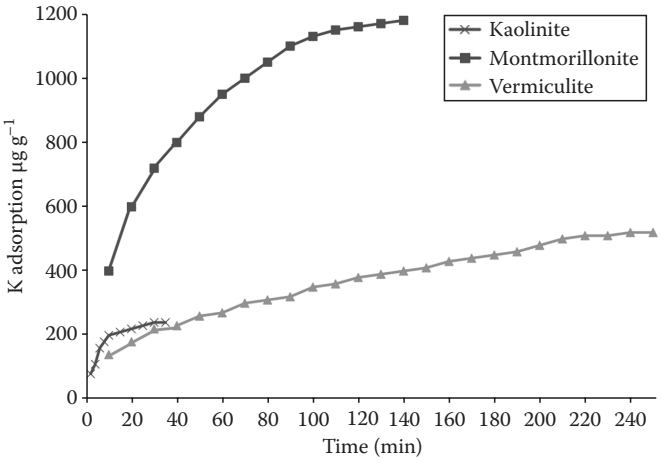

FIGURE 11.10 Potassium adsorption versus time in pure systems. (From Sparks, D.L., and P.M. Jardine. 1984. Soil Sci. 138:115–122. With permission of Wolters Kluwer.)

are available for ionic exchange. With montmorillonite, the inner peripheral space is not held together by H bonds, but instead is able to swell with adequate hydration and thus allow for rapid passage of ions into the interlayer space. Malcolm and Kennedy (1969) found that the rate of Ba exchange on kaolinite and montmorillonite was rapid with 75% of the total exchange occurring in 3 s.

Kinetics of K exchange on vermiculitic and micaceous minerals tends to be extremely slow. Both are 2:1 phyllosilicates with peripheral spaces that impede many ion-exchange reactions. Micaceous minerals typically have a more restrictive interlayer space than vermiculite since the area between layer silicates of the former is selective for certain types of cations (e.g., K^+, Cs^+). Bolt et al. (1963) theorized the existence of three types of binding sites

for K exchange on hydrous mica. The authors hypothesized that slow kinetics were due to internal exchange sites, rapid kinetics to external planar sites, and intermediate kinetics to edge sites.

11.3.3.2 Potassium Fixation

The phenomenon of K fixation or retention significantly affects K availability. The fact that fixation processes are limited to interlayer ions, such as K^+, has been explained in terms of the good fit of K^+ ions (the crystalline radius and coordination number are ideal) in an area created by holes and adjacent oxygen layers (Barshad, 1951). The important forces involved in interlayer reactions in clays are electrostatic attractions between the negatively charged layers and the positive interlayer ions, and expansive forces due to ion hydration (Kittrick, 1966).

The degree of K fixation in clays and soils depends on the type of clay mineral and its charge density, the degree of interlayering, the moisture content, the concentration of K^+ ions as well as the concentration of competing cations, and the pH of the ambient solution bathing the clay or soil (Rich, 1968; Sparks and Huang, 1985).

The major clay minerals responsible for K fixation are montmorillonite, vermiculite, and weathered micas. In acid soils, the principal clay mineral responsible for K fixation is dioctahedral vermiculite. Weathered micas fix K under moist as well as dry conditions, whereas some montmorillonites fix K only under dry conditions (Rich, 1968).

The degree of K fixation is strongly influenced by the charge density on the layer silicate. Those with high charge density fix more K than those with low charge density (Walker, 1957). Weir (1965) noted that K fixation by montmorillonites is limited unless the charge density of the clays is high. Low charge montmorillonite (Wyoming) stays at 1.5 nm when K saturated, unless it is heated (Laffer et al., 1966). Schwertmann (1962a, 1962b) noted that soil montmorillonites have a greater capacity to fix K than do many specimen montmorillonites. Soil montmorillonites have higher charge density and a greater probability of having wedge positions near mica-like zones where the selectivity for K is high (Rich, 1968).

The importance of interlayer hydroxy Al and hydroxy Fe^{3+} material on K fixation was first noted in the classic work of Rich and Obenshain (1955). They theorized that hydroxy Al and hydroxy Fe^{3+} interlayer groups acted as props to decrease K fixation. This theory was later corroborated in the work of Rich and Black (1964) who found that the introduction of hydroxy Al groups into Libby vermiculite increased the Gapon selectivity coefficient (k_G) from 5.7 to 11.1×10^{-2} L $mmol^{-1/2}$.

Wetting and drying as well as freezing and thawing can significantly affect K fixation (Hanway and Scott, 1957; McLean and Simon, 1958; Cook and Hutcheson, 1960). The degree of K fixation or release on wetting or drying is dependent on the type of colloid present and the level of K^+ ions in the soil solution.

Potassium fixation by 2:1 clay minerals may be strongly influenced by the kind of adsorbed cations or the anions within the system. In studies with the silicate ion, Mortland and Gieseking (1951) found that montmorillonite clays dried with K_2SiO_3 were altered in their swelling properties and fixed K in large amounts. Hydrous mica clays also fixed large amounts of K that could not be removed with boiling HNO_3.

Volk (1934) observed a marked increase in K fixation in soils where pH was raised to about 9 or 10 with Na_2CO_3. Martin et al. (1946) showed that at pH values up to 2.5 there was no fixation; between pH 2.5 and 5.5, the amount of K fixation increased very rapidly. Above pH 5.5, fixation increased more slowly. These differences in K fixation with pH were discussed by Thomas and Hipp (1968). At pH values >5.5, Al^{3+} cations precipitate as hydroxy polycations, which increase in the number of OH groups as pH increases, until they have a form like gibbsite (Thomas, 1960). At this pH (~8), Al^{3+} does not neutralize the charge on the clay and cannot prevent K fixation. Below pH 5.5, Al^{3+} and $Al(OH)_x$ species dominate. Below pH 3.5, H_3O^+ predominates (Coleman and Harward, 1953; Thomas and Hipp, 1968).

The increase in K fixation between pH 5.5 and 7.0 can be ascribed to the decreased numbers of $Al(OH)_x$ species, which decrease K fixation (Rich and Obenshain, 1955; Rich, 1960, 1964; Rich and Black, 1964). At low pH, the lack of K fixation is probably due to large numbers of H_3O^+ and their ability to replace K as well (Rich, 1964; Rich and Black, 1964).

11.3.3.3 Potassium Release

The release of K from micas proceeds by two processes: (1) the transformation of K-bearing micas to expansible 2:1 layer silicates by exchanging the K with hydrated cations and (2) the dissolution of the micas followed by the formation of weathering products. The relative importance of these two mechanisms depends on the stability of micas and the nature of soil environments (Sparks and Huang, 1985).

Release of K from feldspars appears to involve a rapid exchange with H, which creates a thin layer of hydrolyzed aluminosilicate. This residual layer ranges in thickness from several to a few tens of nanometers and seems to cause the initial nonstoichiometric release of alkali and alkaline earths, relative to Si and Al. Following this step, there is continued dissolution, which removes hyperfine particles. After these are removed, further dissolution breaks down the outer surface of the residual layer at the same rate that alkalis are replaced by H at the interface between fresh mineral surfaces and the residual layer. This releases all constituents to the solution. Release is now stoichiometric. Thus, the weathering of feldspars appears to be a surface-controlled reaction (Sparks, 1989).

A number of physiochemical and mineralogical factors govern the release of K from micas by both cation exchange reactions and dissolution processes. These include tetrahedral rotation and cell dimensions, degree of tetrahedral tilting, hydroxyl orientation, chemical composition, particle size, structural imperfections, degree of K depletion, layer charge alterations and associated reactions, hydronium ions, biological activity, inorganic cations, wetting and drying, and other factors (Sparks and Huang, 1985). This review will focus on the latter four factors.

Biological activity promotes K release from micas (Mortland et al., 1956; Boyle et al., 1967; Sawhney and Voight, 1969;

Weed et al., 1969). The organisms deplete the K in the soil solution, and their action may be analogous to that of tetraphenylboron (TPB) in artificial weathering of micas. Furthermore, the overall action of organisms is more complex when organic acids are produced (Boyle et al., 1967; Spyridakis et al., 1967; Sawhney and Voight, 1969).

The importance of organic acids in weathering of rock-forming minerals has been recognized for a long time (Sprengel, 1826; Bolton, 1882; Huang and Keller, 1970). All soils contain small but measurable amounts of biochemical compounds such as organic acids. Furthermore, since the time required for soil formation can extend over a period of centuries, the cumulative effect in a soil of even very small quantities of chelating agents will be considerable. The influence of oxalic and citric acids on the dynamics of K release from micas and feldspars was studied by Song and Huang (1988). They found that the sequence of K release from K-bearing minerals by oxalic and citric acids is biotite > microcline orthoclase > muscovite.

The activity of K^+ ions in soil solution around mica particles greatly influences the release of K from micas by cation exchange. When the K level is less than the critical value, K is replaced from the interlayer by other cations from the solution. On the contrary, when the K level is greater than the critical value, the mica expansible 2:1 mineral takes K from the solution. The critical K level is highly mineral dependent, being much higher for the trioctahedral minerals (Smith and Scott 1966; Newman, 1969; von Reichenbach, 1973; Henderson et al., 1976). The critical levels for muscovite are so low that even the K impurities in laboratory chemicals or dissolved from glassware are often sufficient to prevent any K release (Scott and Smith, 1966).

The nature and concentration of the replacing cations also influences the critical K level of the cations tested in Cl^- solutions. Rausell-Colom et al. (1965) found the critical K levels decreased in the order $Ba^{2+} > Mg^{2+} > Ca^{2+} \approx Sr^{2+}$ for the same concentration of these ions and with a constant mica particle size. The activity of all of these replacing ions in the solution phase must be much greater than that of the K for significant K release to occur. The activity of various cations in the soil solution is governed by other minerals in the soil systems, by pedogenic processes, and by anthropogenic activities.

The release of K upon drying a soil is related to the clay fraction (Scott and Hanway, 1960). When a soil is dried, the degree of rotation of weathered soil minerals, such as micas, may be changed. Thus, the K–O bond may be modified. Dehydration of interlayer cations may permit a redistribution of interlayer cations, because Ca could now compete with K for wedge sites. This seems to account for the release of K from soils upon drying. Rich (1972) found that Virginia soils, which contain hydroxy Al interlayers and appreciable amounts of K, did not release K upon drying. The presence of the hydroxy Al interlayers may block or retard the interlayer diffusion of K ions and may change the b-dimension of micas, the degree of tetrahedral rotation, and the length and strength of the K–O bond.

Other factors that can affect K release from soils are leaching, redox potential (Eh), and temperature. Leaching promotes the K release from K-bearing minerals by carrying away the reaction products. Therefore, leaching accelerates the transformation of minerals, for example, micas, to expansible 2:1 layer silicates and other weathering products if the chemistry of leaching water favors the reaction.

Redox potential of soils could influence K release from micas since it has been pointed out that the tenacity with which K is held by biotite is greater after oxidation of its structural Fe. It appears that, other factors being equal, the extent of the K release from biotite should be less in soil environments that oxidize Fe than in soil environments that reduce it. Major elements in K-bearing feldspars do not exist in more than one valence state; thus, the prevailing Eh of a soil may not be of direct concern to chemical weathering of the feldspars. However, the weatherability of feldspars can be affected by complexing organic acids that are vulnerable to oxidation. Therefore, the stability of feldspars may be indirectly related to the prevailing Eh of a soil.

Increasing temperature has been shown to increase the rate of K release from biotite (Rausell-Colom et al., 1965) and K feldspars (Rasmussen, 1972). Under conditions of leaching of biotite with 0.1 mol NaCl L^{-1}, the rate of K release appears directly proportional to temperature in the range of 293–323 K (Mortland, 1958). Under similar leaching conditions, Mortland and Ellis (1959) observed that the log of the rate constant for K release from fixed K in vermiculite was directly proportional to the inverse of the absolute temperature.

Preheating of micas to high temperatures (1273 K) prior to TPB extraction (Scott et al., 1973) was found to enhance the rate of K extraction from muscovite, to decrease the rate for biotite, and to have little effect on phlogopite, except at very high temperatures. The decrease in K release from biotite by preheating is presumably because of oxidation of Fe at high temperatures. The more rapid rate with muscovite following heating remains unexplained.

11.3.3.4 Leaching of Potassium in Soils

Soil solution K is either leached or sorbed by plants or soils. A number of factors influence the movement of K in soils, including the cation exchange capacity (CEC), soil pH and liming, method and rate of K application, and K absorption by plants (Terry and McCants, 1968; Sparks, 1980).

The ability of a soil to retain applied K is very dependent on the CEC of the soil. Thus, the amount of clay and SOM in the soil strongly influences the degree of K leaching. Soils with higher CEC have a greater ability to retain added K, whereas leaching of K is often a problem on sandy soils (Sparks and Huang, 1985).

Retention of K can often be enhanced in sandy, Atlantic Coastal Plain soils after application of lime, since in such variable charge soils, the CEC is increased as soil pH is increased. Nolan and Pritchett (1960) found that liming a Lakeland fine sand soil (thermic, coated *Typic Quartzipsamment*) to pH 6–6.5 caused maximum retentivity of applied K. Potassium was replaced by Ca on the exchange complex at higher levels of limestone application. Less leaching of K occurred at pH 6.0–6.5 due to enhanced substitution of K for Ca than for Al, which was more abundant at low pH.

Lutrick (1963) found that K leaching occurred on unlimed but not on limed areas when 112–224 kg K ha^{-1} was applied on a Eustis loamy fine sand (sandy, siliceous, thermic Psammentic Paleudult).

Movement of applied K has been related to the method of application. Nolan and Pritchett (1960) compared banded and broadcast placement of KCl applied at several rates to Arredondo fine sand (loamy, siliceous, hyperthermic Grossarenic Paleudult) in lysimeters under winter and summer crops. For the low rate of application, cumulative K removal for both placements was only about 5.0 kg ha^{-1}.

A number of investigations have been conducted to determine the relationship of crop uptake and the rate of K application to leaching of K. Jackson and Thomas (1960) applied up to 524 kg K ha^{-1} prior to planting sweet potatoes (*Ipomoea batatas* L.) on Norfolk sandy loam (fine loamy, siliceous, thermic *Typic Paleudult*). At harvest time, soil and plant K exceeded applied K at the 131 and 262 kg K ha^{-1} rates. However, at the 524 kg K ha^{-1} rate, 38 kg K was unaccounted for by soil and plant K. This deficiency of K was attributed to leaching below sampling depths. During a 2 year study with corn (*Zea mays* L.) on two Dothan (*Typic Paleudult*) soils of Virginia, Sparks et al. (1980) found that 83 and 249 kg of applied K ha^{-1} increased the exchangeable K in the E and B21t horizons of the two soils. These increases were ascribed to leaching of applied K. The magnitude of leaching varied directly with rate of K application. No accumulation of K was found in the top 0.76 m of Leon sand (sandy, siliceous, thermic Aeric Haplaquod) after 40 year of heavy K fertilization (Blue et al., 1955).

11.3.4 Assessing Potassium Extractability and Availability

The extractability and availability of soil and plant K can be assessed by using chemical extractants to quantify the various forms of soil K, soil test extractants, quantity/intensity (*Q/I*) analyses, and plant analysis.

11.3.4.1 Chemical Extractants for Soil K Forms

Methods to determine total K and the other alkali elements in soils use acids or a high temperature fusion to decompose the soil. The most widely employed digestion techniques for total elements in soils and minerals have used combinations of HF and either H_2SO_4 or $HClO_4$ (Helmke and Sparks, 1996).

Exchangeable K is that K that is typically extracted with a neutral normal salt, usually 1.0 M NH_4OAc minus the water soluble K (Knudsen et al., 1982). In soils that are not saline, levels of water soluble K are minimal and can be ignored. However, in saline soils, the levels of water soluble K should be determined from a saturated extract or some similar extract and subtracted from the amount of K determined using NH_4OAc.

It should be noted that in soils that contain weathered vermiculitic and micaceous minerals wedge zones can be present that contain K. This K is not accessible to large index cations such as Ca and Mg, but can be extracted by NH_4, which is of similar size to K. For example, in soils that contain wedge zones, NH_4OAc will extract more K than an extractant like 1 M $CaCl_2$. It is debatable whether this K is truly exchangeable. Thus, in soils containing wedge zones, exchangeable K could be overestimated with NH_4OAc (Sparks and Huang, 1985; Helmke and Sparks, 1996).

There are a number of chemical methods that can be employed to extract nonexchangeable K. These include boiling HNO_3, H_2SO_4, hot HCl, electroultrafiltration, Na TPB with EDTA, and ion-exchange resins such as H and Ca saturated resins (Hunter and Pratt, 1957; Martin and Sparks, 1985; Helmke and Sparks, 1996).

The most commonly used method for extraction of nonexchangeable K is the boiling HNO_3 technique. Most researchers that use this method boil the soil in M HNO_3 for 10 min over a flame, transfer the slurry to a filter, leach the soil with dilute HNO_3, and then determine the concentration in the filtrate. One of the problems with boiling for only 10 min over a flame is that it is difficult to be precise about the correct boiling time, the time it takes for boiling to occur, and the vigor of boiling (Martin and Sparks, 1985). Some workers have attempted to diminish these problems by using a 386 K oil bath for 25 min, including heating time (Pratt, 1965). This modification is particularly useful when large numbers of samples are being analyzed. Of course, one of the major concerns with using a boiling HNO_3 procedure is the potential to cause partial dissolution of mineral forms of K.

Other researchers have used continuous leaching of the soil with dilute acids such as 0.01 M HCl or with dilute salts such as 0.1 M NaCl, repeated extractions with 3, 0.3, and 0.03 M NaCl, Sr salts, hot $MgCl_2$, and sodium cobaltinitrite (Martin and Sparks, 1985).

Cation-exchange resins saturated with H or Ca also have been widely used to measure nonexchangeable K. These resins have high CECs and when saturated with an appropriate cation and mixed with soil and with a dilute solution, they will adsorb released K. One of the major advantages of using cation-exchange resins to extract K is that they act as a sink for the released K and thus prevent an inhibition of further K release. This is a problem with many batch methods that employ dilute acids and electrolytes. One major disadvantage of cation-exchange resins for extracting K is that the resins are expensive and the procedure is time-consuming and tedious.

In order for electrolyte and acid solutions and cation-exchange resins to be effective in extracting K, the K concentration in the solution phase must be kept very low, or K release must be inhibited (Rausell-Colom et al., 1965; Wells and Norrish, 1968; Feigenbaum et al., 1981; Martin and Sparks, 1983, 1985). The critical concentration above which release is inhibited is 4 mg L^{-1} for soils in general, 2.3–16.8 mg L^{-1} for trioctahedral micas in dilute solution, and as low as <0.1 mg L^{-1} for muscovite and illite (Smith and Scott, 1966; Martin and Sparks, 1985). A low enough concentration of solution K can be maintained by employing a continuous flowing extracting or exchanging solution, cation-exchange resins, or Na TPB (Scott et al., 1960).

One can quantitatively analyze for mineral K (K feldspars and micas) by using a selective dissolution method employing $Na_2S_2O_7$ fusion. The technique and method for calculating the

quantities of K feldspars and micas can be found in Helmke and Sparks (1996). A semiquantitative approach for measuring mineral K is to subtract the quantity of nonexchangeable K, using the boiling HNO_3 procedure, from the quantity of total K, using the HF digestion method. One also can quantify K feldspars in the sand fraction of soil, using petrographic analyses (Parker et al., 1989b).

11.3.4.2 Soil Tests for Potassium

Soil test extractants for K were developed to easily and rapidly measure K in soils and to estimate K availability. Based on the amounts of extractable K, recommendations that are based on field test calibrations can then be made on the amount of K that is needed to maximize plant yields. Soil tests for K usually estimate the quantity of solution and exchangeable K, and since acids are usually employed as extractants, some nonexchangeable and mineral K is also extracted (Wolf and Beegle, 1991). The soil tests used to measure extractable K in the United States include Mehlich-1 and Mehlich-3 procedures in the northeastern and southeastern United States, the Morgan and modified Morgan procedures in parts of the northeastern United States, the 1 M NH_4OAc at pH 7 procedure in the north-central United States, and the ammonium bicarbonate-DTPA extraction in the western United States. Procedures for these soil tests are fully described in Helmke and Sparks (1996) and Chapter 14.

11.3.4.3 *Q*/*I* Analysis

Schofield (1947) proposed that the ratio of the activity of cations such as K and Ca was defined by the relation $a_K/(a_{Ca})^{1/2}$ where a is the ion activity. He appears to have been the first person to apply the concepts of quantity (Q) and intensity (I) to the mineral nutrient status of soils (Schofield, 1955).

Beckett (1964a), following the consideration of the Ratio law (Schofield, 1947), suggested that the I of K in a soil at equilibrium with its soil solution could best be defined by the ratio $a_K/(a_{Ca} + a_{Mg})^{1/2}$ of the soil solution. This equilibrium activity ratio for K or AR^K (Beckett, 1964a) has often been used as a measure of K availability to plants (Sumner and Marques, 1966; le Roux and Sumner, 1968).

Beckett (1964c) suggested that exchangeable K is held by two distinct mechanisms. The majority is held by general force fields comparable with those that hold exchangeable Na or Ca. A small proportion is held at sites offering a specific binding force for K but not for Ca and Mg. The electrochemical potential of exchangeable K in the diffuse double layer dictates the chemical potential of K in the soil solution. The K activity is also affected by the difference in electrical potential across the diffuse double layer that surrounds the exchange complex. Thus, no simple relationship exists between the activity of K in soil solution and quantity of K on the exchange phase (San Valentin et al., 1973). Moss (1967) and Lee (1973) note that a soil with a given complement of exchangeable K, Ca, and Mg gives rise to an activity ratio for K (AR^K) in the equilibrium soil solution that will be characteristic of that soil and independent of the soil-to-solution ratio and total electrolyte concentration. Moss (1967) noted that the ratio depends only on K saturation and the strength of adsorption of cations.

However, the relation of the amount of exchangeable K to AR^K must be specified to accurately describe the K status of a soil. Beckett (1964b) noted that different soils showing the same value of AR^K may not possess the same capacity for maintaining AR^K while K is removed by plant roots. Therefore, one must include not only the current potential of K in the labile pool but also the form of Q/I or the way in which potential depends on quantity of labile K present. These findings brought about the classic Q/I curves where the ratio of $a_K/(a_{Ca} + a_{Mg})^{1/2}$ is related to the change in exchangeable K to obtain the effect of quantity (exchangeable K) on intensity. The Q/I concept has been widely promulgated in the scientific literature to investigate the K status of soils (Evangelou et al., 1994).

The traditional method for Q/I analyses involves equilibrating a soil with solutions containing a constant amount of $CaCl_2$ and increasing the amounts of KCl (Beckett, 1964a). The soil gains or loses K to achieve the characteristic AR^K of the soil or remains unchanged if its AR^K is the same as the equilibrating solution. The AR^K values are then plotted versus the gain or loss of K to form the characteristic Q/I curve. From the Q/I plot, one can obtain several parameters to characterize the K status of a soil. The AR^K when the Q factor or ΔK equals zero is a measure of the degree of K availability at equilibrium or AR_e^K. The value of ΔK when $AR^K = 0$ is a measure of labile or exchangeable K in soils ($\Delta K°$). The slope of the linear portion of the curve gives the potential buffering capacity of K (PBC^K) and is proportional to the CEC of the soil. The number of specific sites for K (K_x) is the difference between the intercept of the curved and linear portion of the Q/I plot at $AR^K = 0$ (Beckett, 1964b; Sparks and Liebhardt, 1981; Evangelou et al., 1994).

The traditional method described above is too time-consuming for routine analyses. Advances in ion-selective electrode (ISE) technology have allowed for more rapid Q/I analysis (Evangelou et al., 1994). Parra and Torrent (1983) developed an ISE simplified Q/I method whereby a single K-ISE in an electrochemical cell with liquid junction was employed to quantitate the K concentration (C_K) in equilibrated soil suspensions based on a successive addition procedure. The values of AR^K were estimated based on the expression, $AR^K = (11.5 - 0.3b)\ C_K + 22 \times 10^{-6}$, where b is the CEC ($cmol_c\ kg^{-1}$) based on the weight of the soil samples used. The method of Parra and Torrent (1983) is quicker than the traditional Q/I method because equilibration time is reduced to 10 min compared to 24 h for the traditional method. Parra and Torrent (1983) achieved results with their modified procedure that were comparable to the traditional method. Wang et al. (1988) modified the procedure of Parra and Torrent (1983) by making direct measurements of CR_K (concentration ratio: $C_K/(C_{Ca+Mg})^{1/2}$) values with Ca and K-ISEs in an electrochemical cell with or without liquid junction.

11.3.4.4 Plant K Analysis

Plant K analysis will not be discussed in any detail in this review. For extensive discussions on plant analysis, the reviewer

TABLE 11.9 Critical K Concentrations in Agronomic Crops

Crop	Time of Sampling	Plant Part	Critical Concentration[a]
Sugarbeet		Blade	10
Cotton		Leaves	<9–15
Wheat	Jointing (GS6)	Total tops	20–25
	Early boot (GS9)	Total tops	15–20
Rice	Flag leaf to mid-tillering		10–14
Corn	At tassel	Ear leaf	19
	At tassel	Leaves	17–27
	At silk	Sixth leaf from base	13
	At silk	Leaf opposite and just below ear shoot	20
Grain sorghum	Full heading	Second blade below apex	18
Alfalfa		Whole top	8–22
Red clover		Tops	15–22.5
Bermudagrass		Tops	13–15
Orchardgrass		Tops	23–25
Tall fescue		Tops	24–38
Kentucky bluegrass		Tops	16–20

Source: Westerman, R.L. (ed.). 1990. Soil testing and plant analysis. SSSA, Madison, WI. With permission of the Soil Science Society of America.

[a] Critical concentration is that nutrient concentration at which plant growth begins to decrease in comparison with plants above the critical concentration.

is referred to chapters in Westerman (1990). Table 11.9 lists the critical level or concentration of K for various agronomic crops. These levels are usually determined by relating yield (e.g., percentage of the maximum yield or growth rate) to nutrient concentration (g kg^{-1}) for a specific plant part sampled at a given stage of development (Munson and Nelson, 1990). This method is based on the principle that if an element such as K is deficient in a plant, growth rates and yield will be decreased. If one adds increasing amounts of K, the concentration of the element in the plant or plant part increases until an optimum level is attained. Using this approach, growth or yield is expressed as a percentage of the maximum. The zone between the deficient and optimum concentration can be referred to as the transition zone (Ulrich and Hills, 1967). Ulrich and Hills (1967) referred to the transition zone as the zone between nutrient concentrations that produced a 20% reduction in growth or yield and continues to those that cause optimum or 100% in the maximum yield. Dow and Roberts (1982) refer to this latter zone as the critical range where researchers select the yield reduction and nutrient concentrations that are acceptable.

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11.4 Bioavailability of Calcium, Magnesium, Sulfur, and Silicon

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William L. Pan

11.4.1 Introduction

Calcium, Mg, and S are essential mineral elements that are classified as macronutrients. While these three elements generally accumulate in plant tissues in higher concentrations (1.5–35 g kg^{-1}) (Table 11.10) than the micronutrients, they are not as commonly limiting in crop production as N, P, and K. Yet, when the soil bioavailability of Ca, Mg, and S is low, crop yield and quality can be suboptimal, depending on crop species and environmental conditions. Although Si is an essential element in the classical sense for diatoms and algal species of the genera Chrysophyceae and Equisetaceae (Epstein, 1999), it is considered a "beneficial" or "quasiessential" element for many other plant species, most notably rice (*Oryza sativa* L.) and sugarcane (*Saccharum officinarum* L.) (Epstein, 1994).

TABLE 11.10 Calcium and Magnesium Concentrations in Plant Tissue Considered Adequate for Plant Growth

		Range of Concentration		
		Ca	Mg	S
Plant	Tissue	g kg^{-1} Tissue		
Maize	Ear leaf	2.1–10.0	2.0–4.0	1.2–2.5
Rice	Leaves (tillering)	1.6–3.9	1.6–3.9	0.9–3.8
Wheat	Leaves (heading)	2.0–5.0	1.5–5.0	1.5–4.0
Soybean	Leaves	3.6–20.0	2.6–10.0	2.0–4.0
Peanut	Leaves and stem	7.5–20.0	3.0–7.5	2.0–3.0
Cotton	Leaves	19.0–35.0	3.0–7.5	2.9–15.0
Fruit trees	Leaves	14.0–21.0	4.1–6.8	1.3–3.0

Sources: Ca and Mg data adapted from Clark, R., Physiological aspects of calcium, magnesium, and molybdenum deficiencies in plants, in F. Adams (ed.), *Soil Acidity and Liming*, SSSA, Madison, WI, 1984, pp. 99–170; S data compiled from Asher, C.J. et al., Sulfur nutrition of tropical annual crops, in G.J. Blair and A.R. Till (eds.), *Sulfur in South East Asian and South Pacific Agriculture*, The University of New England, Armidale, New South Wales, Australia, 1983, pp. 54–64; Fox, R.L. and Blair, G.J., Plant response to sulfur in tropical soils, in M.A. Tabatabai (ed.), *Sulfur in Agriculture*, ASA, Madison, WI, 1986, pp. 405–434; Kamprath, E.J. and Jones, U.S., Plant response to sulfur in the Southeastern United States, in M.A. Tabatabai (ed.), *Sulfur in Agriculture*, ASA, Madison, WI, 1986, pp. 323–343; Jones, M.B., Sulfur availability indexes, in M.A. Tabatabai (ed.), *Sulfur in Agriculture*, ASA, Madison, WI, 1986, pp. 549–566; Tiwari, K.N., *Sulphur Agric.*, 14, 29, 1990.

The bioavailability of Ca, Mg, S, and Si is governed by the following factors: (1) parent material, (2) ion-exchange reactions, (3) biological transformations, (4) losses from the crop root zone by leaching and crop removal from the field, and (5) replenishment via atmospheric deposition, fertilizer, and soil amendments. Factors influencing Ca and Mg bioavailability are collectively discussed due to the similarity in soil chemical and plant nutritional behavior of these two elements. In contrast, S and Si chemistry in soils and plant nutrition are distinctly different, and are discussed separately in the latter half of the section.

11.4.2 Calcium and Magnesium

11.4.2.1 Overview of Calcium and Magnesium Nutrition

General reviews of the function of Ca and Mg in plants have been written by Clark (1984), Hanson (1984), and Poovaiah and Reddy (1996). A large proportion of Ca is found as Ca pectates in cell walls for structural rigidity, or as Ca oxalate and other organic acids in the apoplasm or vacuoles (Kinzel, 1989; Borchert, 1990). Calcium functions in plants include maintenance of membrane integrity (Caldwell and Haug, 1981) and cell wall stability (Konno et al., 1984), root (Poovaiah and Reddy, 1996) and shoot (Slocum and Roux, 1983) gravitropism, callose deposition (Lerchl et al., 1989), and regulation of several enzymes including α-amylase (Mitsui et al., 1984), protein kinases (Raghothama et al., 1987), and ATPases (Clarkson and Hanson, 1980).

Magnesium functions as an enzyme activator, in addition to serving as the coordinating central cation in the chlorophyll molecule. Magnesium activates numerous plant enzymes by bridging enzymes with ligand groups of substrates to optimize geometric conformation of enzyme systems involving the transfer of phosphate or carboxyl groups (Marschner, 1995). Systems activated by Mg include chlorophyll biosynthesis (Walker and Weinstein, 1991), chlorophyll degradation (Langmeier et al., 1993), photosynthesis (Pierce, 1986), protein synthesis (Cammarano et al., 1972), ATP synthesis (Lin and Nobel, 1971), and ATPases (Balke and Hodges, 1975), some of which are involved in phloem loading of sucrose (Williams and Hall, 1987).

11.4.2.2 Occurrence of Soil Calcium and Magnesium

Calcium and Mg occur in soils primarily in mineral forms and as ions on the exchange complex or in the soil solution. Little Ca or Mg occurs in organic complexes in soils (Mokwunye and Melsted, 1972). The relative amounts of Ca derived from parent materials rank as follows: calcareous sedimentary rock > basic igneous rock > acid igneous rock (Jenny, 1941). Parent materials rank with respect to Mg contents: basic igneous rock > acid igneous rock > sedimentary rock (Metson, 1974). Generally, soils with the highest 2:1 lattice clay content have the highest Mg contents (Mokwunye and Melsted, 1972). Contents of Ca and Mg in soils are presented in Table 11.11.

TABLE 11.11 Contents of Calcium and Magnesium in Various Soils

	Content		
	Ca	Mg	Source
Soil Type	($g\ kg^{-1}$)		
Temperate soils	0.7–36	1.2–15	Brady (1974)
Humid region soil	4	3	Brady (1974)
Arid region soil	10	6	Brady (1974)
Peat soils	1.1–48.3		Brady (1974)
Muck soils		0.7–5.7	Millar (1955)

11.4.2.3 Additions and Losses of Soil Calcium and Magnesium

Calcium and Mg accession by soils from atmospheric deposition may be significant in comparison to that removed in crop and forest plants (Johnson and Todd, 1987). Calcium and Mg depositions from precipitation in a Tennessee forest were 6.3 and 0.7 kg ha^{-1} $year^{-1}$, respectively (Johnson and Todd, 1987). Hedin et al. (1994) estimated atmospheric Ca depositions for Sweden, the northeastern United States, and the Netherlands in the 1990s to be 0.5, 1.0, and 4.2 kg Ca ha^{-1} $year^{-1}$, respectively. Atmospheric deposition of Mg and Ca has garnered more interest lately because of its potential to increase soil inorganic C and thereby reduce atmospheric CO_2 and global warming. Goddard et al. (2007, 2009) reported the highest deposition in the United States to be 1.0–1.4 kg Mg ha^{-1} $year^{-1}$ in the Pacific Northwest and coastal Florida and to be 2.5–3.6 kg Ca ha^{-1} $year^{-1}$ in the central Midwest–Great Plains region.

Considerable amounts of Ca and Mg are added to soils in the form of limestone (21%–32% Ca, 3%–12% Mg), fertilizers, and animal manures. Fertilizers used to specifically supply Ca to soils include gypsum (22% Ca) and calcium nitrate (19% Ca). Calcium may also be added to the soil incidentally while supplying P as superphosphates (14%–20% Ca). Common Mg-containing fertilizers include Epsom salts (10% Mg) and sulfate of potash magnesia (11% Mg).

Loss of Ca and Mg from the soil occurs through leaching and crop removal. Leaching losses of Ca and Mg from an aspen forest (*Populus tremuloides* Michx.) on *Typic Fragiochrept* soils averaged 39 and 9 kg ha^{-1} $year^{-1}$, respectively (Silkworth and Grigal, 1982). Cropping with perennial species reduces leaching losses in comparison to annuals. Calcium and Mg leaching losses were 193 and 104 kg ha^{-1}, respectively, from a continuous maize (*Zea mays* L.) rotation but only 64 and 48 kg ha^{-1} from a bluegrass (*Poa pratensis*) sod (Bolton et al., 1970). The application of Ca generally increases the leaching of Mg (Pratt and Harding, 1957), partly because the adsorption affinity for Ca is greater than that for Mg in non-vermiculitic soils (Hunsaker and Pratt, 1971). Leaching of Ca and Mg is accelerated by acidification, resulting from the nitrification of ammoniacal N sources (Schwab et al., 1989; Darusman et al., 1991). Under acid conditions, Al^{3+} and H^+ ions displace Ca^{2+} and Mg^{2+} from the exchange complex enabling leaching to occur.

Plant removals of Ca and Mg from the soil are dependent on the plant species and genotype and the harvested fraction that is removed from the field. The Ca concentration of plants varies considerably, but one generalization can be made: the Ca concentration of dicots, legumes, and crucifers (12–18 g kg^{-1}) is far greater than the 4 g kg^{-1} Ca typically found in grasses (Parker and Truog, 1920). In contrast, the Mg concentration of these groups of plants differs only slightly (~2–4 g kg^{-1}). Several authors have provided compilations of plant mineral composition that may be useful in estimating crop removal of Ca and Mg (Truog, 1918; Beeson, 1941). Magnesium removals were 5, 7, 8, and 16 kg Mg ha^{-1} for snap beans (*Phaseolus vulgare* L.), okra (*Hibiscus esculentus* L.), white potatoes (*Solanum tuberosum* L.), and sweet potatoes (*Ipomoea batatas* (L.) Lam.), respectively (Prince, 1951). More recently, representative uptakes and removals of Ca and Mg for several crops were reported by Buo1 (1995). Crop removal was in the range of 1–30 kg Ca or Mg ha^{-1} $year^{-1}$. Spring wheat (*Triticum aestivum* L.) accumulated 35 kg Ca ha^{-1} and 13 kg Mg ha^{-1}, whereas sugar beets (*Beta vulgaris* L.) accumulated 104 kg Ca ha^{-1} and 44 kg Mg ha^{-1} (Strebel and Duynisveld, 1989). Barber (1984) reported the total uptake of Mg by maize to be 45 kg ha^{-1}.

Hardwood tree species accumulate substantial amounts of Ca. For example, a mixed oak (*Quercus* sp.) stand grown on *Typic Paleudult* soils contained 1090 kg Ca ha^{-1} (16 kg Ca ha^{-1} $year^{-1}$) in the aboveground plant parts when harvested (Johnson and Todd, 1987). Loblolly pine (*Pinus taeda* L.) grown on the same soils removed only 196 kg Ca ha^{-1}. Both species removed about 45 kg Mg ha^{-1} from the soil (0.6 and 1.5 kg Mg ha^{-1} $year^{-1}$ for mixed oak and pine, respectively). In a more temperate climate, aspen removed 1034 kg Ca ha^{-1} and 95 kg Mg ha^{-1} from *Typic Fragiochrept* soils in northeastern Minnesota (Silkworth and Grigal, 1982).

11.4.2.4 Factors Affecting Availability of Soil Calcium and Magnesium

The activities of Ca and Mg in the soil solution, which directly influence the rates of uptake into plant roots, are dependent on the level of exchangeable cations (Albrecht, 1941) and the type of colloid. Organic matter and 1:1 clays retain Ca less tightly than 2:1 clay minerals, resulting in greater Ca availability at any given level of Ca saturation (Allaway, 1945; Mehlich and Colwell, 1945; Mehlich, 1946).

The affinity of cations for the exchange complex is dependent on the mineralogy of the colloid. For instance, the affinities of Ca and Mg for montmorillonite are similar, but the affinity of Mg for vermiculite is much greater than the affinity of Ca (Wild and Keay, 1964). Soils with exchange complexes arising from organic matter, peat, allophane, kaolinite, and oxides of Fe and Al have a higher affinity for Ca than for Mg (Hunsaker and Pratt, 1971).

The relative abundance of basic cations on the exchange complex affects the plant availability of these ions. Bear et al. (1945) asserted that the ideal base saturation of the exchange complex was 65% of Ca, 10% of Mg, and 5% of K. This concept was termed the basic cation saturation ratio. Although this ideology of soil test interpretation was widely adopted in the Midwestern United States for making fertilizer and lime recommendations (McLean and Brown, 1984), subsequent research demonstrated that a fairly broad range of basic cation saturations would produce equivalent crop yields (Hunter, 1949; Giddens and Toth, 1951; Key et al., 1962; Simson et al., 1979; Osemwota et al., 2007).

The degree of Ca saturation needed to provide sufficient plant-available Ca to crops is dependent on the colloid. Kamprath (1984) concluded from the results of a number of studies that a Ca saturation of about 25%–30% and an exchangeable Ca level of 1.0 $cmol_c$ kg^{-1} in highly weathered soils, dominated by kaolinitic clays and Fe/Al oxides, were adequate for supplying the Ca requirement of most plants. However, other factors such as Al may still limit plant growth at this level of Ca saturation. Soil solution Ca levels in acid soils ranging from 0.38 to 9.3 mM were reported by Kamprath (1978). The soil solution Ca level required for optimum growth of tropical legumes was 0.125 mM, much lower than the 2.0 mM required by temperate legumes (Kamprath, 1978). The soil solution Ca concentration necessary for maximizing cotton (*Gossypium hirsutum* L.) root growth was between 0.04 and 0.34 mM (Howard and Adams, 1965; Adams and Moore, 1983).

11.4.2.5 Calcium and Magnesium Soil–Plant Relationships

The transport of Ca and Mg ions to the root surface occurs by mass flow and diffusion. The soil solution composition and transpiration have been used to estimate the contribution of mass flow to the movement of these ions to plant roots (Barber, 1962). The difference between total nutrient accumulation in the plant and the estimate of that supplied by mass flow gives the relative contribution of diffusion and root interception. From these estimates, Barber (1962) recognized that mass flow could supply more than the required amount of Ca to plant roots of some soil–plant systems, resulting in a buildup of Ca in the rhizosphere that was observed in subsequent experiments (Barber and Ozanne, 1970). He also surmised that in situations where plant Ca demand is high and soil solution Ca is low, the supply of Ca to plant roots can be diffusion limited (Barber, 1962), resulting in a depletion of soluble Ca around the roots (Barber and Ozanne, 1970). Similarly, the mode of Mg transport is cropping system dependent. While mass flow could account for the Mg accumulated by wheat, a majority of Mg moving to sugar beet roots occurred by diffusion (Strebel and Duynisveld, 1989).

The presence of Ca is required throughout the root profile to maintain the integrity of root cell membranes and nutrient uptake (Haynes and Robbins, 1948). Insufficient Ca limits rooting into the subsoil of many Ultisols (Adams and Moore, 1983) and Oxisols (Ritchey et al., 1982) limiting the volume of soil explored and crop access to soil moisture supplies (Sumner et al., 1986; Sumner, 1995). Subsoil horizons in these soils may also be Al and H toxic (Adams and Moore, 1983). The Ca concentration of the soil solution needed to obtain maximum soybean (*Glycine max* (L.) Merr.) root growth increases as pH decreases and Al activity increases (Lund, 1970). The Ca/Al molar ratio of the

soil solution was determined to be an excellent indicator of the potential for Al stress in tree species (Cronan and Grigal, 1995).

The effects of liming on soil Ca levels are initially confined to the zone of incorporation (Ritchey et al., 1980; Pavan et al., 1984, 1987). However, gypsum, phosphogypsum, and soluble Ca applications are effective at providing Ca deep into the soil profile. Forty-four weeks after application, soil Ca was increased in the upper 20 cm of a tropical Inceptisol, but phosphogypsum and $CaCl_2$ increased exchangeable Ca to a depth of 80 cm (Pavan et al., 1987). Growth of alfalfa (*Medicago sativa* L.) was increased in an Appling coarse sandy loam (*Typic Hapludult*) by a surface application of gypsum, which increased subsoil Ca and decreased soluble Al (Sumner et al., 1986; Sumner and Carter, 1988; Sumner, 1995).

Low supplies of Ca inhibit the nodulation, growth, and N fixation of bacteria associated with the roots of legumes (Albrecht, 1931; McCalla, 1937). No N fixation occurs unless the Ca saturation is >40% (Albrecht, 1937). The number of nodules and the amount of N fixed increased to 97% Ca saturation. The number of nodules per plant was positively correlated with the total Ca content of the primary root (Sartain and Kamprath, 1978). The Ca requirement for nodulation is greater at low pH and greater than that for the host plant (Alva et al., 1990). Calcium concentration of 0.5 mM maximized nodule number and weight at pH > 5, but 2.5 mM Ca was required at pH 4.5.

The ratio of Ca and Mg to other cations in the soil solution is important in Ca and Mg sufficiency to the plant. Maximum root length of cotton occurred when the activity of Ca exceeded approximately 15% of the total cation activity in the soil solution (Adams, 1966) and when exchangeable Ca was 13% or more of the total exchangeable cations (Howard and Adams, 1965; Adams and Moore, 1983). These relationships were nearly identical for the two soils examined even though the clay mineralogy of one soil was kaolinitic and that of the other was vermiculitic. Other crops respond similarly to the relative activity of Ca in the soil solution. Root growth of soybean (Lund, 1970) and loblolly pine (Lyle and Adams, 1971) were maximized when the ratio of Ca activity to total cation activity in the soil solution exceeded 10%–20%. Magnesium activity expressed as a function of total cation activity in the soil solution was closely correlated with ryegrass (*Lolium perenne* L.) Mg concentration (Salmon, 1964).

Calcium has low phloem mobility, which results in low Ca redistribution from older plant tissues to growing meristems (Jeschke and Pate, 1991), thereby imposing heavy reliance on concurrent Ca uptake and xylem transport to support new growth and development of vegetative and reproductive tissues (Morard et al., 1996). Plant organs with low rates of transpiration (e.g., new leaves, fruits, tubers) and low rates of xylem flow exhibit Ca deficiency disorders such as pod rot in peanut (*Arachis hypogaea* L.) (Cox et al., 1982; Sumner et al., 1988), internal brown spot in potato (Tzeng et al., 1986), blossom end rot in tomato (*Lycopersicon esculentum* Mill.) (Geraldson, 1957), bitter pit in apple (*Malus* sp.) (Perring, 1986), cork spot in pear (*Pyrus communis* L.) (Raese and Drake, 1993), and blackheart in celery (*Apium graveolens* L.) (Geraldson, 1954). Although low soil Ca levels may increase the frequency and severity of Ca deficiency in these crops, the deficiency is more a function of poor Ca translocation within the plant than of low soil Ca levels.

Calcium uptake and translocation occur at greater rates in actively growing meristematic regions than older root sections (Clarkson, 1984; Marschner, 1995). As a result, soil Ca availability must be optimized in the root zone at the time of active root development (Kratzke and Palta, 1986). Since environmental stresses that curtail root meristematic development can inhibit Ca uptake and translocation to shoot meristems, temperature and moisture stresses can exacerbate low soil Ca availability by imposing transient Ca deficiencies during critical periods of crop development. These environmental stresses by soil–Ca interactions explain why these Ca-related disorders are only displayed in some growing seasons. Foliar and fruit sprays, as well as maintenance of adequate soil Ca, are required to completely alleviate Ca deficiency disorders in sensitive crops (Geraldson, 1954, 1957; Raese and Drake, 1993).

11.4.2.6 Crop Response to Calcium and Magnesium Availability

Optimum soil Ca levels for maximizing yield and quality of peanuts are quite high, 538 kg ha^{-1} for small-seeded cultivars, and 1600 kg ha^{-1} for large-seeded cultivars (Walker et al., 1979; Gaines et al., 1989). Adsorption of Ca for kernel development occurs through the shell. Small-seeded cultivars have relatively more surface area per unit mass for Ca adsorption than large-seeded cultivars, hence the lower soil Ca requirement (Sumner et al., 1988). Reduced peanut yield and quality with low soil Ca are, partly due to destruction of pods by *Pythium* and *Rhizoctonia* fungal pathogens (Hallock and Garren, 1968).

Low Mg uptake by forage grasses can induce grass tetany in ruminants (Grunes et al., 1970), while low Ca in wheat forage leads to wheat pasture poisoning (Bohman et al., 1983). Low rates of Mg and Ca uptake due to suboptimal soil Mg and Ca availability can be exacerbated by high K (Thill and George, 1975; Ohno and Grunes, 1985), low soil temperatures (Miyasaka and Grunes, 1990), low P availability (Reinbott and Blevins, 1994), and wet soil conditions (Karlen et al., 1980). A survey of the incidence of grass tetany in the United States showed greater appearance of the problem in areas where soil parent material is naturally low in Mg and in cooler climates (Kubota et al., 1980). This study concurred with earlier findings of a greater incidence of grass tetany when the Mg concentration in forages is < 2.0 g Mg kg^{-1} and the K/(Ca + Mg) equivalent ratio is > 2.2 (Kemp and 't Hart, 1957).

Exchangeable Mg levels are often poorly related to crop yield response to applied Mg. Incongruities between exchangeable Mg and crop response primarily arise from two sources: a pool of available Mg in the A horizon soil that is not exchangeable, and an accumulation of available Mg below the A horizon. Nonexchangeable Mg may be an important source of plant-available Mg in some soils. Prince and Toth (1937) noted that only about 3%–4% of the total Mg content of Sassafras loam soil was exchangeable, suggesting fixation of Mg in an insoluble form in

the colloidal fraction of the soil. Substantial plant uptake of nonexchangeable Mg occurred in five Coastal Plain soils where only 4%–9% of the total Mg content was in the exchangeable form (Rice and Kamprath, 1968). An additional 4%–10% of the total soil Mg content was extractable with dilute acid and was termed nonexchangeable, but plant available.

Significant fixation of Mg occurred in Oxisols and Ultisols when limed to pH above 7 (Sumner et al., 1978; Grove et al., 1981). Magnesium fixation was nearly 80% in a Bradson soil (*Typic Hapludult*) limed to a pH of 7.2 (Grove et al., 1981). Subsurface accumulations of Mg may also satisfy crop requirements for Mg. Adams and Hartzog (1980) noted that Mg accumulated in the subsoil of Ultisols could explain the lack of crop growth response to applied Mg on soils with extremely low exchangeable Mg in the topsoil. Exchangeable Mg levels were 10-fold greater in the subsoil (60–120 cm) of Wagram loamy sand (Arenic Kandiudult) than in the surface 40 cm (Schmidt and Cox, 1992).

Magnesium deficiencies are intensified by high levels of K or Ca (Welte and Werner, 1963). Severe Mg deficiency of potato and tobacco (*Nicotiana tabacum* L.) and mild Mg deficiencies of sugar beet and barley (*Hordeum vulgare* L.) occurred with heavy applications of K, even though exchangeable Mg levels were considered adequate (Walsh and O'Donohoe, 1945). Magnesium deficiency of citrus occurred when the Mg:K ratio was less than 2.5:1 (Pratt et a1., 1957). Magnesium deficiency of alfalfa occurred when Mg comprised <6% of the exchangeable cations (Prince et al., 1947). Similarly, Mg deficiency of sudangrass (*Sorghum sudanense* [Piper] Stapf) and clover (*Trifolium repens* L.) occurred when soils had <4% of the CEC occupied by Mg (Adams and Henderson, 1962), and in citrus when Mg was <4%–8% of the CEC (Martin and Page, 1969). Exchangeable Mg in excess of 10% of the CEC generally ensures that Mg availability to crops will not be limiting.

When Mg fertilizer applications are made to the soil surface, as in orchards or pastures, or to crops with high Mg requirements, high-solubility fertilizers are more effective than low-solubility materials (Boynton, 1947; Camp, 1947). For example, $MgSO_4$ and MgO increased grapefruit (*Citrus paradise* Macfad.) leaf Mg and alleviated visual symptoms of Mg deficiency within 9 months, whereas effects of $MgCO_3$ were not detected for more than 24 months (Koo, 1971). McMurtrey (1931) reported that considerably more dolomitic limestone was needed than soluble Mg fertilizer to prevent Mg deficiency in tobacco. Foliar applications of $MgSO_4$ can be more effective than soil applications of Mg in correcting Mg deficiency (Scott and Scott, 1951).

11.4.3 Sulfur

11.4.3.1 Overview of Sulfur Nutrition

Sulfur functions in plants have been reviewed by Duke and Reisenauer (1986), DeKok et al. (1993), and Marschner (1995). Sulfur is a structural constituent of organic compounds, some of which are uniquely synthesized by plants, providing animals with essential amino acids (methionine and cysteine) required to synthesize S-containing proteins. Disulfide bonding plays an important role in regulating the 3D conformation of proteins, affecting enzyme function. Sulfur is also contained in vitamins and coenzymes (thiamin, biotin, coenzyme A, and lipoic acid) (Mengel and Kirkby, 1982; Marschner, 1995). Other S-containing compounds include glutathione, an antioxidant (Bergmann and Rennenberg, 1993), and phytochelatin (Grill et al., 1987) as well as glucosinolates, which can serve as natural plant protectants (Schnug, 1993).

11.4.3.2 Occurrence of Soil Sulfur

Soil S exists in organic compounds, and adsorbed and soil solution SO_4^{2-}. Temperate region soils ordinarily contain between 0.1 and 2.0 g S kg^{-1} (Brady, 1974). Representative soils from arid regions contain more S than those from humid regions (0.8 and 0.4 mg kg^{-1}, respectively) (Brady, 1974). The predominant mineral form of S in arid soils is gypsum. Organic S comprises most of the S in most soils (>90% of the total) (Table 11.12). The C:S and N:S ratios of mineral soils vary. The organic pool is composed of three major sources of S (ester sulfates, amino acid S, and C bonded S). Ester sulfate is considerably more labile than C bonded S and is considered an important source of plant-available S. Ester sulfate and C bonded S accounted for 53% and 14% of total organic S, respectively, in 48 surface soils of Ghana (Acquaye and Kang, 1987). Ester sulfate ranged from 35% to 52% of total S in 54 Canadian soils (Bettany et al., 1973), from 20% to 65% in 6 Brazilian soils, and 43% to 60% in 6 Iowa soils (Neptune et al., 1975). Commonly, more than 30% of the total organic S in soils is not identified as either ester sulfate or C bonded S (Neptune et al., 1975; Acquaye and Kang, 1987). Amino acid S has been reported to account for 21%–31% of the total organic S content of two Australian soils (Freney et al., 1972) and 19%–31% of C bonded S in four mineral soils of Scotland (Scott et al., 1981).

Adsorbed SO_4^{2-} occurs on the positively charged exchange sites at the edges of clay minerals, organic matter, and Fe and Al oxides (Chao et al., 1962). The SO_4^{2-} adsorption capacity of a soil is decreased by increased soil pH and P content (Ensminger, 1954;

TABLE 11.12 Total-S, Organic-S, and C:N:S Ratio of Selected Mineral Soils

Origin	Total-S (mg kg^{-1})	Organic-S (mg kg^{-1})	C:N:S[a]	Reference
Saskatchewan, Canada	296	291	79:7.3:1.0	Bettany et al. (1973)
Iowa, U.S.A	319	305	92:8.3:1.0	Neptune et al. (1975)
Oregon, U.S.A	247	235	144:10:1.0	Harward et al. (1962)
Brazil, South America	166	146	139:7.1:1.0	Neptune et al. (1975)
Ghana, Africa	129	121	66:6.8:1.0	Acquaye and Kang (1987)
New Zealand	717	640	91:8.0:1.0	Perrot and Sarathchandra (1987)

[a] Organic C and S for all entries. Total N for all entries, except organic-N for Bettany et al. (1973).

Kamprath et al., 1956). Ultisols, Alfisols, and Oxisols have a high adsorption capacity due to an abundance of Fe and Al oxides and typically low pH. Binding is due to both electrostatic attraction and ligand exchange mechanisms (Marsh et al., 1987; Marcano-Martinez and McBride, 1989) and is highly dependent on the occurrence of positive charge on the soil colloids. Sulfate adsorption occurs rapidly, with nearly complete adsorption in minutes (Rajan, 1978) to days (Marcano-Martinez and McBride, 1989). However, a slower second stage of SO_4^{2-} adsorption also exists, rendering initially adsorbed SO_4^{2-} less available over time (Barrow and Shaw, 1977). Sulfate retention in acid soils is enhanced by Ca (Barrow, 1972; Ryden and Syers, 1976). Marcano-Martinez and McBride (1989) proposed that the stimulation in SO_4 adsorption arose from the bonding of a SO_4–Ca complex to the oxide surface by an O ligand and attraction of the Ca to a negatively charged hydroxyl.

11.4.3.3 Additions and Losses of Sulfur

Major sources of atmospheric S are oceans (24% of the total), soils (35%), volcanic activity (7%), and industry (35%) (Noggle et al., 1986). Sulfur accretion in soils occurs through direct adsorption of S gases and as rainfall. Distance from the source of S determines the amount of deposition. Sulfur in rainfall in Hawaii was exponentially related to distance from the ocean, averaging from 24 to 1 kg S ha^{-1} $year^{-1}$ from the coast to 24 km inland (Hue et al., 1990). As much as 168 kg S ha^{-1} was deposited on soils near industry, whereas urban and rural locations generally received <15 kg S ha^{-1} (Olson and Rehm, 1986). However, clean air legislation in the United States has substantially decreased S emissions from electric utilities and industrial boilers lowering S deposition >30% in the Northeast and Midwest (USEPA, 2010). Although industrial S emissions continue to be reduced in many industrialized countries, thus reducing S deposition (Schnug, 1991), S deposition in some countries remain quite high (Wang et al., 2004). Areas distant from the sea and devoid of industrial sources may have rainfall concentration of <0.1 mg L^{-1} (<0.1 kg S ha^{-1} per 100 mm rainfall) (Fox and Blair, 1986).

The replacement of ordinary superphosphate (12% S) with concentrated superphosphate (1% S) beginning in the late 1940s as the most common P source resulted in an increase in the occurrence of crop S deficiencies in the southern United States (Mehring and Lundstrom, 1938; Jordan, 1964). The use of gypsum as a Ca source for peanuts is another example of incidental S applications to soils. Nutritive applications of S are most frequently applied with N sources. The primary source of S in both liquid and solid N fertilizers is ammonium sulfate (24% S). Ammonium bisulfite (32% S) and thiosulfate (26% S) are also used to provide S in liquid fertilizers. Sulfur sources used in solid fertilizers are potassium sulfate (18% S), potassium magnesium sulfate (23% S), magnesium sulfate (14% S), and ordinary superphosphate. Elemental S is also used sometimes as a slow release source of nutritive S. The S becomes available to plants when the elemental S is oxidized by bacteria to SO_4^{2-} (Starkey, 1966). Oxidation rate is dependent on the size of the S particles, temperature, and moisture (Burns, 1967).

The retention of fertilizer S in surface soils is dependent on rainfall. Nearly 50% of the SO_4^{2-} added to maize was lost from the soil profile by leaching in the subhumid savannah of West Africa (1500 mm rainfall), whereas 100% of that added to a soil in the semiarid savannah (640 mm rainfall) remained in the soil profile to a depth of 105 cm (Friesen, 1991). Nearly all of 56 kg SO_4^{2-} added to Wagram loamy sand (Arenic Paleudult) was leached from the upper 0.45 m of soil with 445 mm of rainfall in 180 days (Rhue and Kamprath, 1973). Leaching losses (24 kg S ha^{-1} $year^{-1}$) exceeded crop removal (15 kg S ha^{-1} $year^{-1}$) even with S inputs from the atmosphere, crop seed, and fertilizer of 37 kg S ha^{-1} $year^{-1}$ and rainfall of 660 mm $year^{-1}$ in clay loam *Typic Eutrochrept* in central Sweden (Kirchmann et al., 1996). Liming and P fertilization decrease S adsorption and increase SO_4-S leaching (Bolan et al., 1988).

Crop removal of S varies by species. Cruciferous forages, alfalfa, and rapeseed (*Brassica napus* L.) accumulate large amounts of S, about 70 kg S ha^{-1} (Spencer, 1975). Sugarcane, coffee (*Coffea arabica* L.), and coconut (*Cocos nucifera* L.) accumulate moderate amounts of S (50 kg S ha^{-1}) (Spencer, 1975), while field crops and forages accumulate between 20 and 30 kg S ha^{-1} annually (Hoeft and Fox, 1986; Kamprath and Jones, 1986).

11.4.3.4 Factors Affecting the Availability of Soil Sulfur

Sulfate uptake by plants from the rooting solution can be saturated at relatively low concentrations of SO_4^{2-}. Soybean growth was optimized with 0.23 mM SO_4-S in nutrient solution (Elkins and Ensminger, 1971). Wheat achieved maximum S accumulation at 0.01 mM SO_4-S in solution (Reisenauer, 1969), while Fox and Blair (1986) concluded that approximately 0.14 mM SO_4-S was required in the soil solution to optimize growth of some tropical and subtropical crops. Early growth of eight agronomic crops was maximized at 0.06 mM in nutrient solution (Hitsuda et al., 2005). Soil reactions that buffer SO_4^{2-} concentrations above these critical soil solution levels are required to optimize S availability. Replenishment of SO_4^{2-} in the soil solution from organic and adsorbed sources is important in determining S supply to the plant (Ribeiro et al., 2001).

Extractable S fluctuates during the year. Tan et al. (1994b) reported that SO_4^{2-} and C-bonded S were inversely related throughout the year in three New Zealand pasture soils (Inceptisols), with the highest proportions of C-bonded S occurring in the winter and SO_4-S predominating in the spring. Although Watkinson and Kear (1996b) found SO_4-S to be constant throughout the year, in contrast to Tan et al. (1994b), they found extractable organic S concentrations to increase in the fall and winter in agreement with the prior study. Conservation tillage was suspected of limiting organic S mineralization in a silt loam Mollisol, resulting in S deficiency of maize (Rehm, 2005).

Sulfate adsorption is negligible in surface soils because little adsorption occurs at soil pH and phosphate levels conducive to crop plant growth (Kamprath et al., 1956). Therefore, most of the effective SO_4^{2-} adsorption in cultivated soils occurs in acid argillic horizons, which often retain enough S to support plant

growth. The range in water soluble SO_4-S concentrations of surface horizons of Ultisols was 0.09–0.16 mM and in the argillic horizon, 0.20–0.36 mM (Camberato and Kamprath, 1986). The depth of the argillic horizon, in part, determines the plant availability of S accumulated in that soil layer. When the argillic horizon was >0.45 m deep, S fertilization increased the yield of tobacco in 2 of 10 site years on four Ultisols, but S deficiency did not occur when the argillic horizon was within 0.30 m of the soil surface (Smith et al., 1987). Linear decreases in maize earleaf S occurred as depth to the argillic horizon in two Ultisols increased from 0.2 to 1.0 m (Cassel et al., 1996).

The depth of crop rooting also influences the amount of S accessible to the crop in soils with subsoil accumulations of SO_4^{2-}. The amount of SO_4-S available to tobacco increased during the growing season and was greater than that of cotton on Durham coarse sandy loam soil (Paleudult) with <18 kg SO_4-S ha^{-1} in the upper 0.45 m of soil, but >72 kg SO_4-S ha^{-1} below 0.45 m (Kamprath et al., 1957). Differences in rooting between these crops explained the difference in S supply. Tobacco was previously shown to have 20% of its root activity below 0.45 m at 7 weeks after transplanting, whereas cotton had a much shallower root system with only 2% of its root activity at this soil depth 11 weeks after planting.

If root growth is prevented by impeding soil layers or high Al^{3+} levels, response to S may occur on soils with high levels of subsoil SO_4^{2-}. Failure to disrupt the tillage pan in a *Typic Kandiudult* prevented rooting into an SO_4^{2-} rich subsoil, and wheat grain yield was increased by S fertilization (Oates and Kamprath, 1985). On an adjacent soil that was subsoiled to allow rooting below the tillage pan, wheat obtained sufficient S for maximum crop productivity. Aluminum saturations in excess of 50% were implicated in reducing rooting in the SO_4^{2-} rich subsoil of Aquic Hapludult, resulting in an increase in maize yield with S fertilization (Kline et al., 1989). Limited crop rooting due to shallow soils causes S deficiency of maize and alfalfa in the Midwestern United States (Hoeft and Fox, 1986).

Sulfur commonly limits crop production in the subhumid and humid regions of the Pacific Northwest. Low atmospheric deposition of S (6 kg ha^{-1} $year^{-1}$), low S-containing surface irrigation water and basalt, granite, and volcanic ash parent materials have resulted in soils that have low total S content and low S bioavailability (Rasmussen and Kresge, 1986). Sulfur responses in cereals are dependent on having adequate N availability (Koehler, 1965) and high yield potential (Ramig et al., 1975). High rainfall and winter leaching potential in the humid regions of the Western coastal areas coupled with low S deposition create S deficient conditions in cereal, forage, fruit, and vegetable production (Rasmussen and Kresge, 1986). In contrast, arid soils in the western United States with high accumulations of soluble SO_4^{2-}, low leaching potential under nonirrigated conditions, or that are irrigated with high SO_4^{2-}-containing groundwater respond less frequently to S fertilization.

11.4.3.5 Assessing Levels of Soil Sulfur

Although organic S is the predominant form of S in most soils, many studies have demonstrated that total S or organic S are poorly correlated to crop response to applied S. Measures of extractable S, which may include soil solution, exchangeable, and organically bound SO_4^{2-} and S, have been reasonably successful at predicting response to S fertilization. Differences in the chemical extractant, concentration, temperature, and other procedural factors affect the quantity and form of S extracted from the soil (Anderson et al., 1992). The analytical procedure used to determine S in the extract also influences the quantity of S measured. Turbidimetric and anion-exchange chromatography methods measure only solution SO_4^{2-} levels, whereas inductively coupled argon plasma spectrophotometry measures total S in solution, including solution SO_4^{2-}, ester SO_4^{2-}, and soluble organic S (Anderson et al., 1992). The contribution of S in rainfall to the crop (Hoeft et al., 1973) and subsoil SO_4^{2-}, which are not often quantified, may also be reasons why soil S analysis for predicting crop response is not always reliable. An S deficiency risk index based on atmospheric deposition, annual rainfall and soil type, texture, and pH agreed well with the occurrence of reported S deficiency in cereals (McGrath and Zhao, 2007).

Extractable SO_4-S was not a good indicator of S sufficiency on seven silt loam Mollisols in Minnesota (O'Leary and Rehm, 1991). However, the amount of S mineralized during a 4 or 12 week aerobic incubation was related to maize yield response to S fertilization, indicating the importance of organic S to plant-available S in some soils. Approximately 30% of the S extracted from eight field-moist New Zealand soils was in the soluble organic form, while the remainder was SO_4^{2-} (Tan et al., 1994a). Labile organic-S determined S availability in Oxisols with low and medium S adsorption capacity (SAC), but mineral SO_4-S forms determined S availability in high SAC soils (Ribeiro et al., 2001). Extractable organic S is a good predictor of the amount of labile S. Organic S extracted by potassium phosphate was a better predictor of maximum yield in pastoral soils of New Zealand than initial SO_4^{2-}; SO_4^{2-} mineralized during short-term incubation, organic S extracted by calcium phosphate, or organic S extracted by sodium bicarbonate (Watkinson and Kear, 1996a). Potassium phosphate extracted more organic S from high organic matter soils than the commonly used calcium phosphate extractant. Blair et al. (1991) found that extraction with KCl was superior to either calcium phosphate or sodium bicarbonate as an indicator of pasture response to fertilizer S in 18 soils from northern New South Wales, Australia. Critical levels for the three extractants ranged from 6.5 to 8.4 mg kg^{-1}. The bicarbonate extractant in this case was probably inferior to the others because it overestimated the contribution of available S arising from the ester SO_4^{2-} fraction.

11.4.3.6 Crop Response to Sulfur Availability

Sulfur deficiencies occur worldwide, but are most prevalent in areas where S accretions from atmospheric deposition, the S contents of fertilizers and pesticides, and irrigation water are low, and soils are sandy with low soil organic matter content, and rainfall is plentiful (Tisdale et al., 1986).

Numerous examples of crop S deficiencies and responses to S fertilization are presented by Tabatabai (1986). Recently, the

incidence of S deficiency appears to be increasing in the United States as a result of less atmospheric S deposition. Sawyer et al. (2009) in Iowa noted only 3 S deficiencies out of 200 research trials with maize and soybean in 40 years prior to 2005. Since then, about two-thirds of more than 50 maize and of 6 alfalfa trials have responded to S fertilization (Sawyer et al., 2009). Many years of cropping without S fertilization may also contribute to the increased occurrence of S deficiency.

Sulfur deficiencies decrease crop yields and in certain instances also reduce crop nutritional value and quality. Sulfur fertilization of subirrigated meadow vegetation (Nichols et al., 1990) and forage maize (O'Leary and Rehm, 1990) increased dry matter accumulation, but did not affect crop quality. In other instances, S fertilization increased both the protein- and S-containing amino acid content of forages, resulting in increased animal performance (Rendig, 1986). In mixed pastures, S application up to 90 kg S ha^{-1} increased total forage production and the proportion of clover to grass (Jones, 1964). Numerous yield responses of coastal bermudagrass (*Cynodon dactylon* (L.) Pers.) to S fertilization have been documented (Kamprath and Jones, 1986). Alfalfa is the most S responsive crop grown in the Midwest and Northeast regions of the United States (Hoeft and Fox, 1986).

Cyst(e)ine and methionine levels of seeds are increased by S fertilization resulting in more nutritious foods (Rendig, 1986). Baking quality of wheat flour is highly dependent on the S concentration of the grain and is increased by S fertilization (Haneklaus et al., 1992). The S status (Zhao et al., 1995) and baking quality (Zhao et al., 1999) of British wheat decreased substantially in the 12 years after 1981 due to reduced atmospheric S deposition. Bread dough made from S-deficient grain resists extension and has lower extensibility (Moss et al., 1981), which is related to low albumin proteins (Wrigley et al., 1984). Sulfur-containing metabolites influence the flavor of several crops including asparagus (*Asparagus officinalis* L.) and various *Allium* sp. (Schnug, 1990).

11.4.4 Silicon

11.4.4.1 Overview of Silicon Nutrition

The roles of Si in plant nutrition and agriculture have been recently reviewed in Datnoff et al. (2001), Korndörfer and Lepsch (2001), Ma et al. (2001), and Snyder et al. (2007). Uptake of $Si(OH)_4$ (Lewin and Reimann, 1969) appears to be active in Si accumulators such as rice, sugarcane, and bamboo [*Sasa veitchii* (Carrière) Rehder], and passive in others such as oats (*Avena sativa* L.) and other "dryland" Gramineae (Jones and Handreck, 1967), while legumes and other dicots appeared to exclude $Si(OH)_4$. Although concentrations of Si in normal plants range from 1 to 100 g kg^{-1} of dry weight (Epstein, 1999), those in Si accumulators greatly exceed the levels of any essential plant nutrients taken up from the soil (e.g., >200 g Si kg^{-1} dry weight in mature bamboo leaves [Motomura et al., 2002]). Silica gel (hydrated amorphous silica, $SiO_2 \cdot nH_2O$) is present as specialized "skeletal" structures in the epidermal cells and cell walls of many plants (Lewin and Reimann, 1969). These structures when enhanced by Si fertilization may be responsible for increased resistance to plant diseases and insect pests. Solid silica in plant tissue occurs as opal (Jones et al., 1966) in the form of phytoliths, which persist in soil after plant decay.

11.4.4.2 Occurrence of Soil Silicon

Silicon, next to O_2, is the most abundant element in soils, ranging from 2% to 45% and averaging about 31% in the conterminous United States (Shacklette and Boerngen, 1984). Commonly occurring Si minerals include quartz, tridymite, cristobalite, and inorganic and biogenic opal with solubilities ranging from 1 to 70 mg L^{-1} (Wilding et al., 1977). The Si:O ratio is 1:2 in these minerals. Silicon is also a component of other primary and secondary minerals and of the phyllosilicate clay minerals. Silicon occurs in the soil solution as $Si(OH)_4$ at 0.1–0.6 mM levels (Epstein, 1999).

Silicon bioavailability in soil is primarily a function of Si quantity and solubility as determined by weathering and soil pH. $Si(OH)_4$ reacts with Fe, Al, Mn, and other heavy metals to form sparingly soluble silicates (Snyder et al., 2007). $Si(OH)_4$ is sorbed by Fe and Al oxides with the latter sorbing more Si than Fe oxides (Jones and Handreck, 1965). Sorption by both sesquioxides increases with increasing pH (Beckwith and Reeve, 1963; McKeague and Cline, 1963b; Jones and Handreck, 1965). Thus, $Si(OH)_4$ in the soil solution decreases as pH rises (Beckwith and Reeve, 1963, 1964; McKeague and Cline, 1963a, 1963b; Jones and Handreck, 1965). Flooding increases soil solution $Si(OH)_4$, probably due to the reduction of Fe, which releases adsorbed $Si(OH)_4$ (Savant et al., 1997b). Carbonates also sorb Si but not as strongly as sesquioxides (Beckwith and Reeve, 1963). Across 23 paddy soils in China available Si was positively correlated with pH, silt, clay, and $CaCO_3$ content of the soil and negatively correlated with organic matter and amorphous Fe oxide (Liang et al., 1994).

Leaching of $Si(OH)_4$ from the soil profile is a characteristic of soil weathering. Little Si is accrued in soil via atmospheric deposition, but substantial additions may be realized with irrigation. In Hawaii, rainfall and mist Si concentrations were 0.2 and 0.05 mg L^{-1}, respectively, whereas well water contained between 2.5 and 30 mg Si L^{-1} (Fox et al., 1967). From a survey of the literature (Savant et al., 1997a), irrigation water Si concentrations ranged from ~2 to 16 mg Si L^{-1}.

11.4.4.3 Crop Response to Silicon Bioavailability

Silicon application increases crop resistance to disease organisms and insect pests while increasing yield. Rice, sugarcane, and barley show the most consistent response to increased Si bioavailability (Snyder et al., 2007). Beneficial responses occur most often on organic soils (Histisols), highly weathered soils (Ultisols and Oxisols), and sandy Entisols (Datnoff and Rodrigues, 2005).

Silicon increases plant resistance to abiotic stresses including moisture deficit, high temperatures, and salinity (Ma, 2004), while it suppresses several diseases of rice including blast (*Magnaporthe grisea*), brown spot (*Cochliobolus miyabeanus*), and stem rot (*M. salvanii*) (Datnoff and Rodrigues, 2005).

Datnoff (2005) summarized the beneficial effects of Si fertilization in reducing several diseases affecting both warm- and cool-season turfgrasses. Pathogens suppressed include *Bipolaris cynodontis*, *M. grisea*, *Pythium aphanidermatum*, *Rhizoctonia solani*, *Sclerotinia homeocarpa*, and *Sphaerotheca fuliginea*. Reynolds et al. (2009) summarized the indirect and direct impacts of Si augmentation of plants on herbivorous insects. Increased plant Si impacts several insect feeding guilds including lepidopteran borers, folivores, and phloem- and xylem-feeders. Silicon applied to the plant foliage also increased plant resistance to some insect pests (Reynolds et al., 2009).

Yield increases in rice due to Si application ranged from 10% to 30% (Savant et al., 1997b); while in China, wheat was less responsive (4%–9%) than rice (5%–21%) (Liang et al., 1994). These beneficial responses in both crops were partly due to reduced diseases and lodging. Sugarcane responses to Si fertilization in Florida, Hawaii, and Mauritius (Matichenkov and Calvert, 2002) ranged from 17% to 30% in total dry matter and 23% to 58% in sucrose content. Beneficial effects were due to increased disease-, pest-, and frost-resistance. Responses of barley to Si in Russia and England (Snyder et al., 2007) were generally in the range of 10%–20%, but several exceeded 40%.

Slags produced from various metal smelters are often used as sources of Si for crop production. Slag composition can be quite variable in Si concentration ranging from 5%–10% in steel mill to 15%–20% Si in blast furnace slags from pig iron manufacture as well as in other essential elements including Ca, Mg, Mn, and Fe (Savant et al., 1997b). Solubility of Si in slag varies widely (–20% to ~70%) (Savant et al., 1999) with finer particles being more effective than larger pellets as a source of Si for increasing rice plant tissue Si and reducing disease incidence (Datnoff et al., 1992).

Silicon application rates needed to optimize crop yield are substantially higher than those of any other essential plant nutrient. For example, recommended Si fertilization rates (as Ca silicate slag) to optimize rice yield in Florida are 1500 kg Si ha^{-1} at a soil test of <6 mg L^{-1} soil and 1120 kg Si ha^{-1} at 6–24 mg L^{-1} soil (Korndörfer et al., 2001). Suggested rates of slag application for sugarcane production range from 1 to 9 Mg ha^{-1} (approximately 200–1800 kg Si ha^{-1}), dependent on the slag and soil Si concentration (Savant et al., 1999). The high rates of Si application needed to optimize plant bioavailability arise as a result of reduced solubility in the "fertilizer" material, sorption by the soil, and the large quantity needed by the plant. Although significant residual effects of a single Si application have been observed over 5 years of cropping, 50%–75% of that applied was unavailable after 5 years as assessed by chemical and biological techniques (Khalid and Silva, 1978; Khalid et al., 1978), suggesting transformation into unavailable forms. In another study, the residual value of a 3 Mg Si ha^{-1} application for reducing disease and increasing of rice yield in the second growing season was approximately equivalent to 1 Mg Si ha^{-1} applied in that season (Datnoff et al., 1991). Because Si uptake may be as high as 700 kg ha^{-1} for sugarcane, 300 kg ha^{-1} for rice, and 150 kg ha^{-1} for wheat (Snyder et al., 2007), crop removal substantially reduces soil Si (Savant et al., 1997a).

Several soil testing methods to evaluate soil Si sufficiency typically remove a fraction of sorbed Si in addition to water soluble Si. The chemical extractant, solution pH, ionic strength, shaking time, and soil:solution ratio vary among methods and remove different amounts of Si from the soil (Savant et al., 1999). For example, water, phosphate-acetate, acetate, and modified Truog (H_2SO_4) methods were evaluated as potential soil test methods for identifying Si deficient soils for sugarcane production (Fox et al., 1967) with critical values being 9, 50, 20, and 40 mg kg^{-1}, respectively. Although each method extracted different amounts of Si, all methods were equally effective in predicting plant Si accumulation ($r > 0.92$).

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11.5 Bioavailability of Micronutrients

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11.5.1 Introduction

Minor or trace elements include both biologically essential (e.g., Cu, Mn, Fe, B, Ni, Mo, Cl, and Zn) and nonessential (e.g., Pb, Cd, and Hg) elements. The essential elements (for plant, animal, or human nutrition) are required in low concentrations and hence are known as "micronutrients" (Table 11.13). Because the nonessential minor elements are phyto- and/or zootoxic even at low concentrations, they are widely known as "toxic elements" or

TABLE 11.13 Sources of Micronutrients in Soils and Their Functions in Plant and Animal

Micronutrient	Ionic Species in Soil Solution	Sources	Functions
Boron (B)	$H_3BO_3^o$	Fertilizers, rocks, fly ash	Plant: required for cell wall strength and development, cell division, fruit and seed development, sugar transport, and hormone development
Chloride (Cl)	Cl^-	Muriate of potash, micas, feldspars	Plant: controls opening and closing of stomata, balances K in cells, required in photosynthesis, for ionic balance and transport, reduces susceptibility to disease
Cobalt (Co)	Co^{3+}, Co^{2+}, $[Co(H_2O)_6]^{2+}$; $[CoCl_4]^{2-}$	Fertilizers, mafic rock, minerals	Plant: required for N fixation, stem and coleoptiles elongation, leaf disc expansion, curvature of slit stems, opening of hypocotyl hooks, and bud development Nonenzymatic: Cobalamine or vitamin B12—erythropoiesis, granulopoiesis, glucose homeostasis
Copper (Cu)	Cu^{2+}, $Cu(OH)_2^o$, $CuOH^+$, $CuSO_4^o$, $CuCO_3^o$, $Cucl^+$, $CuHCO_3^+$	Fertilizers, fungicides, electrical, paints, pigments, timber treatment, mine tailings	Plant: enzyme activator, major function in: photosynthesis, reproductive stage, respiratory enzymes, indirect role in chlorophyll production, increases sugar content, intensifies color, and improves flavor in fruits and vegetables. Animal: Enzymatic: Cytochrome oxidase—Principal terminal oxidase; Lysyl oxidase—Lysine oxidation; Tyrosinase—Skin pigmentation—Cytocuprein: Superoxide (O_2^-) dismutation. Nonenzymatic: Growth promoter in swine and poultry; lameness control in cattle
Iron (Fe)	Fe^{2+}, $FeCl^+$, $Fe(OH)_2^+$, $FeH_2PO_4^+$, $Fe(OH)_3^-$, $Fe(SO_4)_2^-$, $Fe(OH)_4^{2-}$	Fertilizers, iron core, rocks, minerals	Plants: Promotes formation of chlorophyll, enzyme mechanism operates the respiratory system of cells, reactions involving cell division, energy transfer within the plant, a constituent of certain enzymes and proteins, plant respiration, and plant metabolism, and involved in N fixation
Manganese (Mn)	Mn^{2+}, $MnOH^+$, $MnCl^+$, $MnCO_3^o$, $MnHCO_3^+$, $MnSO_4^o$	Fertilizer, rocks	Plant: role in metabolism of organic acids, activates the reduction of nitrite and hydroxylamine to ammonia, role in enzymes involved in respiration and enzyme synthesis, activator of enzyme reactions such as oxidation/reduction, hydrolysis and direct influence on sunlight conversion in the chloroplast, assimilation of carbon dioxide in photosynthesis, synthesis of chlorophyll and in nitrate assimilation, manganese activates fat forming enzymes, formation of riboflavin, ascorbic acid, and carotene, electron transport during photosynthesis, and involved in the Hill Reaction where water is split during photosynthesis Animal: Enzymatic: Arginase—Urea formation; Pyruvate carboxylase—Pyruvate metabolism
Molybdenum (Mo)	MoO_4^{2-}, $HMoO_4^-$, $H_2MoO_4^o$	Fertilizer	Plant: essential for N fixation and nitrate reduction, converting nitrate into amino acids, conversion of inorganic P into organic forms within the plant Enzymatic: Xanthine oxidase—Purine metabolism; Sulfite oxidase—Sulfite oxidation
Nickel (Ni)	Ni^{2+}, $NiSO_4^o$, $NiHCO_3^+$, $NiCO_3^o$	Alloys, batteries, mine tailings	Plant: required for Fe absorption, participate in N metabolism of legume during the reproductive phase of growth, phytoalexin synthesis, and plant disease resistance Nonenzymatic: Increases bone strength in poultry
Selenium (Se)	$HSeO_3^-$, SeO_4^{2-}, SeO_3^{2-}, $MgSeO_4^o$,	Fertilizers, selenide minerals, recycled electronic devices, sulfide ore	Plant: increases the tolerance of plants to UV-induced oxidative stress, delays senescence, promotes the growth of ageing seedlings, regulates the water status of plants under condition of drought Enzymatic: Glutathione peroxidase—Protection against haemoglobin oxidation. Nonenzymatic: Growth promoter
Zinc (Zn)	Zn^{2+}, $ZnSO_4^o$, $ZnCl^+$, $ZnHCO_3^+$, $ZnCO_3^o$	Fertilizers, galvanizing, dyes, paints, timber treatment, mine tailings	Plant: formation of growth hormones (auxin), seed and grain formation, promotes maturity, protein synthesis and transformation, and consumption of carbohydrates Animal: Enzymatic: carbonic anhydrase—CO_2 formation; regulation of acidity; carboxypeptidase—Protein metabolism; alcohol dehydrogenase—alcohol metabolism; cytocuprein—superoxide (O_2^-) dismutation Nonenzymatic: Eczema control in cattle

"heavy metals" or "heavy metalloids" and include both cationic and anionic forms. Both groups can be toxic to plants, animals, and humans above certain concentrations specific to each element and target biota.

Soil represents the major sink for minor elements released into the biosphere through both geogenic (i.e., weathering or pedogenic) and anthropogenic (i.e., human activities) processes. The mobility and bioavailability of minor elements in soils are affected by adsorption onto mineral surfaces, precipitation as salts, formation of stable complexes with organic compounds, and bioaccumulation and biotransformation by microorganisms (Adriano, 2001). Soil is a biologically active integral component of the terrestrial ecosystem in which higher plants, soil constituents, and soil organisms interact, where the available energy in the form of organic and inorganic compounds promotes microbial activity and microbial weathering processes.

Bioavailability, which refers to how much of an element is available to living biota including plants and soil microorganisms, defines the relationship between its concentration in the terrestrial environment and its level that actually enters the receptor causing either a positive or negative effect on the organism. Bioavailability is species-specific because the dose that reaches an organism's target organs or tissues resulting in a biological response varies among receptors (Stokes et al., 2005). Bioavailability often refers to the extent to which an element can desorb, dissolve, or otherwise dissociate from the solid phase in which it occurs to become accessible (i.e., bioaccessibility) for absorption (Alexander and Alexander, 2000).

Chemical bioavailability is now considered an important environmental consideration because availability may be mitigated once the element comes in contact with the soil or sediment. For this reason, both soil fertility status as well as risk assessment of contaminated sites require quantification of chemical bioavailability as is carried out for other nutrients in fertilizer recommendations and risk calculations (Hrudey et al., 1996). In both fertilizer recommendations and contaminated site assessment, bioavailability, which addresses the fundamental issue of exposure of a receptor (plant) to the element in question, is not dictated by the total element concentration in the soil, but rather by the fraction of the total amount that is biologically available. Consequently for the element to become available, it must be desorbed from the soil particle and transported to the root via the soil solution. The amount of an element in soil that is bioavailable depends on a variety of factors including the properties of both the element and the soil environment (Black, 2002; Adriano et al., 2004).

This chapter covers the following aspects of the essential micronutrients (Cu, Zn, Se, Mo, Fe, Mn, Co, Ni, B, and Cl) in relation to their bioavailability in soils: (1) sources and dynamics, (2) indicators and factors affecting bioavailability, and (3) bioavailability implications to soil testing.

11.5.2 Sources of Micronutrients

Just like the major elements such as P and K, micronutrients reach the soil environment through both pedogenic and anthropogenic processes (Tables 11.14 and 11.15). Most micronutrients

TABLE 11.14 Selected References on Micronutrient Concentrations (g kg^{-1}) in Cattle, Poultry and Swine Manure By-Products, and Municipal Biosolids

Sources	Co	Cu	Mn	Mo	Ni	Fe	Se	Zn	References
Cattle manure	—	0.029	0.372	—	0.009	0.009	—	0.067	de Abreu and Berton (1996)
	—	0.139	—	0.002	0.0008	0.002	0.003	0.191	McBride and Spiers (2001)
	—	0.200	0.700	—	—	—	—	0.800	Eneji et al. (2001)
	0.003	—	0.357	—	0.008	0.005	0.0005	0.164	Raven and Loeppert (1997)
	—	0.016	0.149	—	—	—	—	6.480	Wallingford et al. (1975)
	—	0.037	—	—	0.004	0.003	—	0.153	Nicholson et al. (1999)
	—	0.033	—	—	0.006	0.007	—	0.133	Nicholson et al. (1999)
Poultry manure	—	0.400	1.800	—	—	—	—	2.300	Eneji et al. (2001)
	0.313	—	0.246	—	—	—	—	0.327	Wood et al. (1996)
	0.002	0.743	0.607	0.004	0.010	2.760	0.001	0.501	Jackson et al. (1999)
	0.002	0.031	0.166	0.005	—	—	0.0004	0.158	Capar et al. (1970)
	0.006	0.748	0.956	0.006	0.015	1.095	—	0.718	Moore et al. (1998)
	0.008	0.019	0.271	—	0.014	0.013	—	0.252	Bomke and Lowe (1991)
Swine manure	—	1.338	0.869	—	0.012	0.014	—	1.440	de Abreu and Berton (1996)
		1.000	2.100	—	—	—	—	2.900	Eneji et al. (2001)
	—	1.279	0.197	—	—	—	—	0.231	Mullins et al. (1982)
	—	0.374	—	—	0.007	0.003	—	0.431	Nicholson et al. (1999)
Biosolids	0.017	0.294	6.230	0.011	0.075	48.100	0.001	1.250	Jackson et al. (1999)
	—	0.119	0.214	—	0.015	0.324	—	0.328	de Abreu and Berton (1996)
	—	0.089	0.350	—	4.304	0.085	—	0.354	de Abreu and Berton (1996)
	0.010	1.346	0.194	0.014	—	0.003	0.003	2.132	Capar et al. (1970)
	0.004	—	0.142	—	0.031	0.130	0.001	0.450	Raven and Loeppert (1997)

TABLE 11.15 Total and Water-Soluble Micronutrient Concentration (g kg^{-1}) in Fertilizers, Dairy Cattle, Poultry and Swine Manures, and Biosolids

	Dairy Cattle[a]		Poultry[b]		Swine[a]		Sewage Sludge[c]		NPK (15-30-15)[d] Fertilizer	
Element	Total	Water Soluble	Total	Water Soluble	Total	Water Soluble	Total	Water Soluble	Total	Soluble Water
Co			0.0068	0.0031					—	—
Cu	0.356	0.112	0.656	0.314	0.419	0.130	0.148	0.0044	0.700	0.700
Mn	0.345	0.017	0.274	0.006	0.865	0.014			5.000	5.000
Ni	0.009	0.001	0.0087	0.005	0.012	0.003	0.028	0.0001	—	—
Se	—	—	0.0095	0.0038					—	—
Zn	0.765	0.123	0.246	0.018	1.210	0.023	0.330	0.0016	0.600	0.600
Fe									1.500	1.500
Mo									0.005	0.005

[a] Bolan et al. (2003a).
[b] Jackson and Bertsch (2001).
[c] Henry and Harrison (1992).
[d] McCauley (2009).

occur naturally in soil parent materials, chiefly in forms that are not readily bioavailable for plant uptake. Often the micronutrient concentrations released from the soil by natural pedogenic processes are largely related to the origin and nature of the parent material. On the other hand, micronutrients added through anthropogenic activities including fertilization typically have higher bioavailability (Naidu et al., 1996a). Fertilizer and manure additions to agricultural soils are the major sources supplying micronutrients for plant growth (Tables 11.15 and 11.16). Anthropogenic activities, associated with industrial processes, manufacturing and the disposal of domestic and industrial wastes, also contribute to micronutrient enrichment of soils (Adriano, 2001).

11.5.3 Dynamics of Micronutrients in Soils

Micronutrients undergo both chemical and biological transformations including retention, redox and methylation reactions while they are retained in the soil by sorption, precipitation, and complexation, and removed by plant uptake and leaching. Although most micronutrients are not subject to volatilization losses, Se tends to form gaseous compounds through redox and methylation reactions (Frankenberger and Karlson, 1995). When micronutrient solution concentration is low and sorption surfaces large, sorption/desorption processes will govern the soil solution concentration (Tiller, 1989) while the fate of micronutrients in the soil depends on both soil properties and environmental factors.

11.5.3.1 Chemical Transformation Processes

11.5.3.1.1 Sorption and Complexation

Chemical interactions that contribute to micronutrient retention by soil colloids include sorption and complexation with inorganic and organic ligands. Charged ions are attracted to charged soil surfaces by electrostatic and/or stronger covalent bonds (Mott, 1981), which can be specific or nonspecific in nature (Bolan et al., 1999). In nonspecific adsorption, the ion charge balances that on the soil surface by electrostatic attraction while in specific adsorption, chemical bonds form between the ions and the soil surface (Sposito, 1984). Metal ion binding on soil organic matter (SOM) is strongly pH dependent due to competition between metal ions and protons for the available binding sites and to the effect of pH on the electric charge development on SOM. Detailed descriptions of these processes are presented in Chapters 11 and 19 of *Handbook of Soil Sciences: Properties and Processes*.

11.5.3.1.2 Cation-Exchange Reactions

Although most soils have a net negative charge, this charge plays only a minor role in micronutrient reactions in soil. In general, for ions having the same charge, ions with the larger hydrated radius are selectively adsorbed. The many ion exchange selectivity coefficients reported in the literature have been determined in the presence of ligands but the effects of ion-pair formation and complex ions have been generally ignored. Comparisons between reported selectivity coefficients for various systems and exchange reactions can, therefore, not be made with confidence (Sposito, 1984). Very little information is available on the values of the coefficients for ion exchange between dominant and micronutrient cations in soil–water systems.

11.5.3.1.3 Specific Adsorption at Mineral Surfaces

Although most macronutrient cations are weakly retained by soils in exchangeable form, most micronutrient cations are strongly retained as inner sphere complexes with variable charged surfaces by the formation of covalent bonds. Although specific adsorption in the form of inner sphere complexes with variable charged mineral surfaces occurs most readily for metals that hydrolyze in water, such as most of the transition elements (Cu, Fe, Mn, Co, Zn, Ni) and some other divalent

TABLE 11.16 Micronutrient Content of Some Commonly Occurring Fertilizers Used in Agricultural Production

Micronutrient	Fertilizer Compound	Chemical Formula	Concentration (g kg^{-1})
Boron	Boric acid	H_3BO_3	89
	Borax	$NaB_4O_7 \cdot 10H_2O$	110
		NaB_4O_7	214
	Solubor©		175
Cobalt	Cobalt sulfate heptahydrate	$CoSO_4 \cdot 7H_2O$	210
	Cobalt carbonate	$CoCO_3$	460
	Cobalt amino acid chelate	—	20
	Cobalt chelate	CoEDTA	130
Copper	Copper sulfate monohydrate	$CuSO_4 \cdot H_2O$	390
	Copper sulfate pentahydrate	$CuSO_4 \cdot 5H_2O$	250
	Copper oxide	CuO	750
	Copper oxy-chloride	$CuCl_2 \cdot 3Cu(OH)_2$ or $Cu_2Cl(OH)_3$	590–700
	Copper chloride	$CuCl_2$	170
	Copper chelate	CuEDTA	80–130
Chloride	Potassium chloride (muriate of potash)	KCl	500
Iron	Ferrous sulfate	$FeSO_4 \cdot 7H_2O$	400
	Ferric sulfate	$Fe_2(SO_4)_3 \cdot 4H_2O$	230
	Ferrous oxide	FeO	770
	Ferric oxide	Fe_2O_3	690
	Ferrous ammonium phosphate	$Fe(NH_4)PO_4 \cdot H_2O$	290
	Ferrous ammonium sulfate	$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$	140
	Iron ammonium polyphosphate	$Fe(NH_4)HP_2O_7$	220
	Iron chelates	NaFeEDTA	50–140
		NaFeHEDTA	50–90
		NaFeEDDHA	60
		NaFeDTPA	100
	Iron polyflavonoids	—	90–100
	Iron lignosulfonates	—	50–80
	Iron methoxyphenylpropane	—	50
Manganese	Manganese sulfate	$MnSO_4 \cdot 4H_2O$	230–280
	Manganese chelates	MnEDTA	50–120
	Manganous oxide	MnO	410–680
	Manganese methoxyphenylpropane	MnMPP	100–120
	Manganese carbonate	$MnCO_3$	310
	Manganese chloride	$MnCl_2$	170
	Manganese oxide	MnO_2	630
	Manganese frits	—	100–250
Molybdenum	Ammonium molybdate	$(NH_4)_6Mo_7O_{24} \cdot 2H_2O$	540
	Molybdenum frits	Silicates	20–30
	Molybdenum sulfide	MoS_2	600
	Molybdenum trioxide	MoO_3	660
	Sodium molybdate	$Na_2MoO_4 \cdot 2H_2O$	390
Nickel	Nickel plus	Nickel lignosulfonate	54
	Nickel chloride	$NiCl_2 \cdot 6H_2O$	150
Selenium	Sodium selenite	NaSe	450
	Selenium premix	—	2–4
Zinc	Zinc sulfate monohydrate	$ZnSO_4 \cdot H_2O$	360
	Zinc sulfate heptahydrate	$ZnSO_4 \cdot 7H_2O$	224

(*continued*)

TABLE 11.16 (continued) Micronutrient Content of Some Commonly Occurring Fertilizers Used in Agricultural Production

Micronutrient	Fertilizer Compound	Chemical Formula	Concentration (g kg^{-1})
	Zinc oxy-sulfate	$ZnO–ZnSO_4$	380–500
	Zinc oxide	ZnO	500–800
	Zinc chloride	$ZnCl_2$	500
	Basic zinc sulfate	$ZnSO_4 \cdot 4Zn(OH)_2$	550
	Zinc carbonate	$ZnCO_3$	520
	Zn sulfide	ZnS	670
	Zn frits	—	Varies
	Zinc phosphate	$Zn_3(PO_4)_2$	510
	Zinc chelate	NaZnEDTA	60–140
		NaZnHEDTA	60–100
		NaZnNTA	130
	Zn polyflavonoid	—	100
	Zn ligninsulfonate	—	50

micronutrients, adsorption reactions usually involve the formation of an inner sphere complex between the hydroxo-metal ion and the deprotonated negatively charged surfaces of Al, Mn, and Fe oxides. The relative affinities of the metals tend to follow the *Irving–Williams* order:

$$Cu^{2+} > Zn^{2+} > Ni^{2+} \sim Co^{2+} > Fe^{2+} > Mn^{2+}$$

11.5.3.1.4 Adsorption by Soil Organic Matter

Metals can react with SOM by ion exchange, complexation, and precipitation. Although complexation as inner sphere complexes between the cation and SOM coordinating functional groups is thought to be the most important reaction, the difficulties involved in studying SOM preclude accurate separation of the processes in most experiments. The retention of metals by SOM at pH 5.8 decreases in the order (Schnitzer and Khan, 1978):

$$Fe = Al = Cr = Hg = Pb = Cu > Cd > Zn > Ni > Co > Mn$$

Although multiligand complexes can form with simple organic acids, 1:1 complexes occur mainly with ligands of the structurally complex macromolecules in SOM, but two or more donor atoms in the macromolecule may be involved in the complexation reaction. Because electron donors in SOM are mainly O, N, and S, the important binding groups are as follows: –COOH (carboxyl), –OH (enolic and phenolic), –SH (thiol), $–NH_2$ (amino), =O (carbonyl), and –S (thioether). With increasing pH, carboxyl, phenolic, alcoholic, and carbonyl functional groups dissociate, thereby increasing their affinity for cations. This results in SOM having a high affinity for micronutrients cations.

Micronutrients are known to form organic complexes that affect their sorption onto soil particles (Adriano, 2001; He et al., 2005). For example, Bolan et al. (2003a) demonstrated that the addition of organic manures increased the complexation of Cu in soils. Additionally, they observed that while Cu^{2+} adsorption measured as the change in the total Cu in soil solution was not affected by biosolid addition, Cu complexation measured as the change in free Cu^{2+} concentration, increased with increasing level of biosolid.

Modeling of the binding of metals to humic materials as in MINTEQA2 is in its infancy with most work having been conducted on organic matter dissolved in surface waters rather than on SOM (Susetyo et al., 1991). More research is needed to develop suitable models that quantify metal retention by SOM.

The extent of micronutrients-organic complex formation, however, varies with a number of factors including temperature, steric factors, and concentration. All these interactions are controlled by solution pH and ionic strength, nature of the micronutrients species, dominant cation, and inorganic and organic ligands present in the soil solution.

11.5.3.1.5 Precipitation

At high pH and in the presence of SO_4^{2-}, CO_3^{2-}, OH^-, and HPO_4^{2-}, precipitation appears to be the predominant process when micronutrient cation concentrations are high (Naidu et al., 1996b). This occurs when the ionic product in the solution exceeds the solubility product of that phase. In normal soils, precipitation is not very important, but in heavy metal contaminated soils, the precipitation process can play a major role in remediation, especially under alkaline pH. Increasingly, addition of phosphate is being used to precipitate excessive levels of micronutrients such as Zn (He et al., 2005).

11.5.3.1.6 Leaching and Runoff

Micronutrients occur in solution either as free ions or soluble complexes that are prone to leaching. L'Herroux et al. (1997) showed that repeated applications of swine manure slurry increased the concentrations of Mn, Co, and Zn in drainage water manyfold. Similarly, Moore et al. (1998) found increased soluble Cu and Zn in runoff with increasing metal loading through poultry manure application, obtaining a strong relationship between dissolved organic carbon (DOC) and soluble Cu and Zn in the runoff.

However, pretreating the manure with $Al_2(SO_4)_3$ decreased runoff losses of these micronutrients as a result of sorption onto $Al(OH)_3$ formed upon hydrolysis of $Al_2(SO_4)_3$.

Migration of micronutrients in soils after manure slurry applications is greatly enhanced by DOC (Japenga et al., 1992; del Castilho et al., 1993; Li and Shuman, 1997; Hsu and Lo, 2000). Acidification due to nitrification from applied manures releases micronutrients from the solid phase (Japenga et al., 1992; del Castilho et al., 1993). Thus, while organic matter in manure byproducts may provide some buffer against metal bioavailability, it does not prevent the metal from being more mobile.

11.5.4 Biological Transformation Processes

11.5.4.1 Plant Uptake and Bioaccumulation

Micronutrients are applied to overcome deficiencies, thereby increasing crop production. When micronutrients in soil are deficient, yield responses to fertilizer and manure are often observed due to increased uptake. Typical examples of yield responses to micronutrients in several crops are presented by Mortvedt (1999). Although plant uptake is a major sink for micronutrients, only a small fraction of that applied to soil is ever taken up because the greatest proportion is immobilized.

Microorganisms can bioaccumulate micronutrients from substrates containing very low concentrations. Bacteria produce large quantities of extracellular polymers with anionic properties that remove soluble micronutrients ions from solution (Srinath et al., 2002) while many fungal products, such as glucans, mannans, melanins, chitins, and chitosans can act as efficient biosorption agents (Blackwell et al., 1995). Thus, microorganisms are competitors with plant roots for these nutrients.

11.5.4.2 Oxidation/Reduction

Redox reactions, both chemical and biological, affect the bioavailability of micronutrients such as Fe, Mn, and Se. In agricultural soils, the reduced forms of Fe^{2+} and Mn^{2+} are most available while Se is more available in the oxidized [Se(VI)] form. Because of the great heterogeneity in the pore space of most soils, zones of reducing and oxidizing conditions are often in close proximity to one another allowing roots to access the available forms at different points in the soil. Application of manures to soils that are subject to reducing conditions (very wet) can result in losses of micronutrients such as Mn by leaching (L'Herroux et al., 1997), while micronutrients such as Co sorbed on sesquioxides under oxic conditions (McLaren et al., 1984) can be released due to manure-induced reduction of these oxides. Temporary flooding of alfalfa fields often result in substantial yield decreases due to the induced Mn^{2+} toxicity from the reducing conditions.

11.5.4.3 Methylation/Demethylation

While some metals (As, Hg, and Se) can be methylated and lost by volatilization (Cernansky et al., 2009), none of the plant-essential micronutrients are involved. Thus, this process is only of interest in metal contaminated sites.

11.5.5 Bioavailability of Micronutrients in Soils

11.5.5.1 Definition

The bioavailability of an element in the soil environment is defined as the fraction of the total that is present in the soil solution and on the solid phase that is available to the plant (Naidu et al., 2008). Considerable controversy exists as to "what constitutes the bioavailable fraction," including the definition itself and the methods used for its measurement. For instance, microbiologists often regard the bioavailable fraction as the concentration that can induce a change either in morphology or physiology of the organism, whereas plant scientists regard the plant-available pool as the bioavailable fraction, which is the definition that will be used here. Physical accessibility of micronutrients for uptake occurs either through movement of ions to roots by diffusion and mass flow or through root extension to the site of the nutrient. Chemical accessibility requires that nutrients remain in the soil solution in the form in which they are taken up (Marschner, 1995). Because the transformation of micronutrients in soils is a dynamic process, bioavailability changes with time.

11.5.5.2 Indicators of Bioavailability

Micronutrients occur in various fractions in soils that include the following (Shuman, 1991):

1. Structural components of primary and secondary minerals (e.g., Mn in manganous oxide)
2. Precipitated in inorganic forms, including those occluded by Fe, Al, and Mn oxides (e.g., Zn)
3. Complexed by organic matter (e.g., Cu)
4. Incorporated into organic matter including microbial biomass (e.g., B, Se)
5. Specifically adsorbed onto silicate clay minerals and Fe, Al, and Mn oxides (e.g., Zn)
6. On clay and organic exchange sites
7. Water soluble as free and complexed inorganic and organic ions

Despite only small amounts of micronutrients being present in exchangeable (6) and water soluble fractions (7) from which uptake occurs, they are continuously replenished from other less-soluble fractions, ensuring continuity of supply. Micronutrient bioavailability in soils can be assessed using chemical and biological tests.

11.5.5.2.1 Chemical Tests

11.5.5.2.1.1 Single Extraction A range of chemical extractants including mineral acids (e.g., 1 M HCl), salt solutions (e.g., 0.1 M $CaCl_2$), buffer solutions (e.g., 1 M NH_4OAc), and chelating agents (e.g., DTPA) have been used to predict micronutrient bioavailability in soils (Sutton et al., 1984; Payne et al., 1988; Sims and Johnson, 1991) but chelating agents, such as EDTA and DTPA are usually more reliable (Sims and Johnson, 1991), since they are more effective in removing potentially bioavailable fractions. However, they do not actually measure availability (Beckett et al., 1983a, 1983b). For example, although the

DTPA-extractable Cu was linearly related to Cu application rate, no relation with corn grain or leaf tissue Cu existed (Payne et al., 1988). Nevertheless, because DTPA-extractable micronutrients increase with metal level in soil (Wallingford et al., 1975; Haleem et al., 1992; Martinez and Peu, 2000), which is related to crop uptake (Wallingford et al., 1975; Mullins et al., 1982; Bibak, 1994; Duffera et al., 1999), DTPA-extractable micronutrients and plant uptake may in some cases be fortuitously related (Beckett et al., 1983a, 1983b).

11.5.5.2.1.2 Sequential Fractionation Sequential fractionation schemes are often used to examine the redistribution or partitioning of micronutrients in various chemical forms that include soluble, adsorbed (exchangeable), precipitated, organic, and occluded. Although the extraction procedures vary between chemical fractionation schemes, generally the solubility and bioavailability of micronutrients in soils decrease with each successive step in the scheme (Basta and Gradwohl, 2000). Specific chemical pools measured by chemical fractionation have been correlated with plant uptake and have been successful in predicting micronutrient availability in soils (Shuman, 1991). Because chemical extraction is matrix dependent, validation for different micronutrients sources, such as inorganic fertilizer, and organic biosolid and manure by-products must be carried out.

The diversity of reagents used to extract specific metal forms from soils makes comparison of results difficult (Table 11.17). Even when the same reagent is employed, the efficiency of extraction depends on the nature of sample, its particle size distribution, duration of extraction, pH, temperature, strength of extractant, and solid:solution ratio (Miller et al., 1986). Because chemical reagents used for extraction may themselves alter the indigenous speciation of micronutrients, milder extractants are usually more selective albeit less efficient for specific fractions than more aggressive reagents, which may extract other forms as well (Lake et al., 1984; Ross, 1994).

Redistribution of micronutrients as measured by fractionation techniques depends on their source. While fertilizer-applied micronutrients tend to remain in soluble and exchangeable form, those applied in manure are in the organic-bound form. For example, after fractionation of metal-organic components in a manure-amended soil, del Castilho et al. (1993) found that strongly bound organic–metal complexes (Cu and Zn) were mostly associated with hydrophobic acids (phenols) and neutrals (hydrocarbons) while the weakly bound micronutrients were complexed with hydrophilic neutrals (i.e., carbohydrates).

11.5.5.2.1.3 Diffusive Gradient Thin Film Diffusive gradient thin film techniques physically mimic the removal of metals by a plant by having a layer of chelating resin behind a diffusive layer (usually a gel faced with a filter membrane) that is in contact with the soil solution. This chemically and physically well-defined system introduces a sink for ions in the soil, which results in a concentration gradient in the soil solution adjacent to the device and a consequent supply of ions from the solid phase into the locally depleted solution (Smith et al., 2007).

11.5.5.2.1.4 Isotopic Techniques Methods, such as isotopic dilution and the isotopic exchange kinetics (IEK) method have been shown to measure phytoavailable elements in soils (Hamon et al., 2008; Hedley, 2008). Isotopic dilution techniques consist of spiking soil with the metal before cropping after which the specific activity (isotope:nonisotope ratio) of the plant and soil solution are measured; from this, the amount taken up from the isotopically exchangeable pool can be calculated, allowing for a good estimation of the amount of phytoavailable element.

The IEK technique, which is used to study isotopic exchange as a function of time, can be employed in conjunction with other techniques to describe the transfer of Co (Wendling et al., 2009), Cu (Ma et al., 2006), Zn (Sinaj et al., 1999; Zhang et al., 2006), Ni (Echevarria et al., 1998), and Se (Goodson et al., 2003) in soils and is very useful in describing plant availability in terms of quantity/intensity (*Q*/*I*) concepts (Hamon et al., 2002).

The labile pool of an element in soil, whether determined by radioactive or stable isotopes, can be considered as a relatively unambiguous assessment of the chemical and biological reactivity of that metal in soil compared with fractions isolated by chemical extractants (Hedley, 2008). However, it should be recognized that isotopic exchange determinations are based on the assumption that the added spike (radioisotope or stable isotope) remains 100% available for exchange. Any fixation ("irreversible" sorption) of some of the spike by reactive soil phases will result in an overestimate of the size of the labile pool (Hamon et al., 2002).

11.5.5.2.2 Biological Tests

11.5.5.2.2.1 Phytoavailability Plant availability of micronutrients largely depends on the source, soil type, and plant species (Martinez and Peu, 2000). While the application of micronutrient fertilizers usually increases the uptake of the elements by plants, application of manure by-products can both increase or decrease micronutrient concentrations in plants. For example, addition of farmyard manure increased the uptake of soil Co and Mn by winter wheat (Bibak, 1994), while acidification of soils by manure increased the B and Zn concentrations in the soil solution and uptake by maize (Jahiruddin et al., 2001). On the other hand, three annual of applications of ~24 kg Cu ha^{-1} as Cu-enriched swine manure increased Cu concentration in the corn ear leaf, but did not affect either corn grain yield or grain Cu concentration (Kornegay et al., 1976). Similarly, the uptake of Se from Se-enriched cattle manure was found to be less than that from an inorganic source (Ajwa et al., 1998) and the addition of cattle manure decreased the concentration of borate anions in soil solution and the subsequent plant uptake of B (Yermiyahu et al., 2001).

11.5.5.2.2.2 Microbial Availability Long-term applications of biosolids to agricultural land can reduce microbial activity in soils as a result of high concentrations of micronutrients (McGrath, 1994). In contrast, only limited studies have examined the direct effect of manure-borne micronutrients on microbial activity. Huysman et al. (1994) showed that in soils receiving

TABLE 11.17 Selected References on the Array of Reagents Used to Partition the Chemical Forms of Micronutrients Derived from Various Sources in Soils

		Fraction/Form							
Source	Element	Soluble	Exchangeable	Adsorbed	Organic	Oxide	Carbonate	Residual	Reference
Fertilizers	Zn	1 mol L^{-1} NH_4NO_3 (pH 7.0)			0.1 mol L^{-1} $Na_4P_2O_7$ (pH 10)	0.1 mol L^{-1} $NH_4OH \cdot HCl$ in 0.01 mol L^{-1} HNO_3	1 mol L^{-1} NaOAc pH 5.0		Gonzalez et al. (2008)
	Cu		0.01 $Ca(NO_3)_2$		0.7 M NaOCl (pH 8.5)	0.2 M NH_4O_x, 0.2 Oxalic acid, 0.1 M Ascorbic acid		HNO_3, $HClO_4$, HF (3:1:10)	McLaren and Ritchie (1993)
	B	Hot water							Haddad and Kaldor (1982)
	Mn	H_2O	NH_4OAc						Rayment and Verrall (1980)
	Mn		1 M $MgCl_2$ (pH 7)			0.1 M $NH_2OH \cdot HCl$ (pH 2)	1 M NaOAc (pH 5)		Nádaská et al. (2009)
	Co, Mn		0.01 M $Ca(NO_3)_2$		3% NaOCl (pH 8.5)	0.1 M $NH_2OH \cdot HCl$		HNO_3	Li et al. (2001)
	Ni	H_2O	1 M $MgCl_2$		30% H_2O_2	0.175 M $(NH_4)_2C_2O_4$—0.1 M $H_2C_2O_4$	0.5 M NaOAc + 0.5 M HOAc		Rahmatullah et al. (2001)
	Se	1 M $MgCl_2$		1 M NaH_2PO_4		10 M HF		Acid	Lim and Goh (2005)
Manures	Cu	0.05 M $CaCl_2$		2% CH_3COOH	0.1 M $K_4P_2O_7$	0.175 M $(NH_4)_2C_2O_4$		HCl, HNO_3, HF	Payne et al. (1988)
	Cu	0.5 M $CaCl_2$		2% CH_3COOH	0.1 M $K_4P_2O_7$				Mullins et al. (1982)
	Cd, Cu, Ni, Zn,		1 M $MgCl_2 \cdot 6H_2O$		0.02 M HNO_3; 30% H_2O_2, 3.2 M $(NH_4)_2C_2O_4$	0.04 $NH_2OH \cdot HCl$ in 25% CH_3COOH	1 M NaOAc	HCl, HNO_3	Narwal and Singh (1998)
	Cd, Pb, Zn	H_2O	0.5 M KNO_3		0.05 M NaEDTA	0.5 M NaOH		4 M HNO_3	Pierzynski and Schwab (1993)
	Cd, Cr, Cu, Ni, Pb, Zn	0.1 M $CaCl_2$			0.5 M NaOH		0.05 M NaEDTA		Canet et al. (1997)
	Cd, Pb, Zn	H_2O	1 M $Mg(NO_3)_2$		0.7 M NaOCl	0.1 M $NH_2OH \cdot HCl$ (Mn oxide); 0.2 M $(NH_4)_2C_2O_4$ – 2 M $H_2C_2O_2$ – ascorbic		HCl, HNO_3, HF	Li and Shuman (1997)
	Cu, Zn	1 M NH_4NO_3			H_2O_2	$(NH_4)_2C_2O_4$ – 2 M $H_2C_2O_2$		4 M HNO_3	Han et al. (2001)
	Cu	H_2O	0.5 M $Ca(NO_3)_2$	0.44 CH_3COOH	O.1 M $K_4P_2O_7$	0.275 $(NH_4)_2C_2O_4$	0.1 M $NH_2OH \cdot HCl$	HCl, HNO_3, HF	Miller et al. (1986)

swine manure for 5 years, there was no effect of Cu on anaerobic bacteria or fungal activity, but aerobic Cu-resistant bacteria increased with increasing soil DTPA Cu concentration, indicating that this may provide a sensitive measure of Cu bioavailability in soils. Application of swine and cattle manure slurries to grasslands acidifies soil while increasing total C and N contents, resulting in significant decreases in microbial biomass C and N. This suggests a decrease in the microbial turnover rate of C and N in manure-amended soil, apparently caused by increased solubilization of Cu, Ni, and Zn (Christie and Beattie, 1989). Organic complexation of Cu and other metals in biosolids and manures may be the main reason for the lower level of toxicity to soil biota of this form compared to inorganic salts, indicating that both microbial and plant toxicity is largely controlled by the free metal ion concentration (van Rhee, 1975; Brookes and McGrath, 1984; McGrath, 1994).

11.5.6 Factors Affecting Bioavailability of Micronutrients in Soils

11.5.6.1 Soil Interactions

Properties of the soil and its ambient solution determine the dynamic equilibrium between micronutrients in solution and solid phases, thereby affecting their bioavailability. Micronutrients interact with particulates by metal ion adsorption at surface sites, ion exchange with clay minerals, binding with organic-coated particulate matter or organic colloidal material, and by adsorption of metal–ligand complexes. All of these interactions are controlled by application of various soil amendments, pH, ionic strength, nature of the metal species, dominant cation, and inorganic and organic ligands present in the soil solution.

11.5.6.1.1 pH

Soil pH has a marked effect on metal adsorption increasing from <20% to 100% within the narrow pH range of 3–5 for all metals except those that form oxyanions (Forbes et al., 1976; Kinniburgh and Jackson, 1981; Christensen, 1984; Brümmer et al., 1988; Tiller, 1989; Naidu et al., 1994). This pH range, called the adsorption edge, generally occurs 2–3 pH units below the value of the pK for the hydroxide solubility constant of the hydrated metal ion and is partly a function of the experimental conditions (Barrow, 1986). This pH effect on adsorption of micronutrients depends on initial solution concentration, nature of soil constituents, and metal retention capacity of soils. Increased adsorption of metal ions with increasing pH is due to both increased negative surface charge density (Naidu et al., 1994) and increased concentration of the MOH^+ species in the soil system (Hodgson et al., 1964). As discussed above, at pH values less than the value of the point of zero net charge (pznc), an increase in soil pH leads to a marked increase in the negative electrostatic potential of a variable charge system, which promotes cation adsorption. However, the precise nature of this interaction between metal ions and particle surfaces is unclear as different mechanisms have been proposed to explain the increasing metal adsorption with pH. For example, the rapid increase in adsorption of Zn within the adsorption edge was attributed to abrupt changes in the concentration of $ZnOH^+$ species as the pH increases toward the pK_1 of the hydrolysis of Zn^{2+} (Barrow, 1986).

11.5.6.1.2 Ionic Strength

The effects of ionic strength on the adsorption of metals by soils are not as well understood as those of pH (Petruzzelli et al., 1985; Naidu et al., 1994). The effect of ionic strength on metal adsorption by soils depends on the surface properties of the particles being more pronounced in variable than permanent charge soils. Metal adsorption decreases with increasing ionic strength for permanent charge minerals (Garcia-Miragaya and Page, 1976; Schindler et al., 1987; Boekhold et al., 1993).

11.5.6.1.3 Index Cation and Solution Composition

Cation adsorption by soils is a competitive process in which the degree to which any cation is adsorbed depends on the concentrations and identity of the other cations present (Bolan et al., 1999). This phenomenon has practical implications on the behavior of micronutrients in soils because the concentration of several metal cations (e.g., Na^+, Ca^{2+}, and Mg^{2+}) in soil solution ranges from <0.01 M in Oxisols to >0.1 M in saline sodic soils. Such changes in ionic strength and metal ion concentration can enhance the mobility and, thus, the bioavailability of micronutrients in soils, for example, by liming or gypsum application, both of which increase Ca^{2+} ions that can compete with micronutrients for adsorption sites.

11.5.6.1.4 Inorganic and Organic Ligands

Ligands play important roles in numerous soil chemical processes such as mineral weathering, control of dissolved micronutrient concentrations, and dissolution and plant availability of micronutrients (see Harter and Naidu, 1995). The soil solution also contains inorganic ligand ions such as Cl^-, SO_4^{2-}, PO_4^{3-}, and NO_3^- whose concentrations vary considerably with soil type from >0.1 M in saline to <0.001 M in highly weathered soils. Such variations in ligand ion concentrations modify both the nature and surface interactions of the metal species present, leading to marked variability in metal bioavailability.

Dissolved organic material consists of a range of low molecular weight compounds including water soluble humic and fulvic acids, which are dominant except in the rhizosphere where simple organic compounds may dominate. Despite extensive studies of metal ions with organic matter (Stevenson, 1991), the values of the reaction constants need to be improved because only limited efforts have been directed toward understanding the role of low molecular weight organic acids in the dynamics of metals in the soil solution; this is due partly to the commonly held, but incorrect, belief that such organic material is rapidly degraded, and therefore short-lived, and partly to difficulty assaying the low concentrations of organic acids present. In the vicinity of plant roots, dissolved organic matter concentrations, often reaching millimolar levels, are high due to root exudates and microbial activity (Harter and Naidu, 1995), greatly enhancing the bioavailability and uptake of soil P, Cu, Fe,

Mn, and Zn (Braum and Helmke, 1995). The role of plant and microbial exudates on metal reactions in soils is an area that lacks information and is an active area of research.

11.5.6.2 Soil Amendments

A number of amendments can change micronutrient bioavailability either through mobilization that releases the micronutrient into soil solution for plant uptake or through immobilization where the micronutrient concerned is removed from soil solution either by adsorption, complexation, and precipitation, rendering the micronutrient unavailable for plant uptake and leaching to groundwater.

11.5.6.2.1 Chelating and Complexing Agents

When a micronutrient ion combines with an electron donor containing two or more donor groups, a complex or coordination compound with one or more rings called a micronutrient chelate is formed. A "chelate" (Greek, *chela* meaning claw) is so named because these species can coordinate at several or all positions literally wrapping themselves around a central micronutrient ion. Chelating agents, which have a high affinity for micronutrients ions such as Fe, Cu, and Zn, can be used to enhance the solubilization of micronutrients by the formation of soluble micronutrients chelates such as EDTA, EDHA, DTPA, and EHPG (Table 11.16). The effectiveness of a chelate in mobilizing soil micronutrients depends on several factors, including species, micronutrient:chelate ratio, thermodynamic stability constants, presence of competing cations, soil pH, stability of the micronutrient–chelate complex, the ageing, and the extent of micronutrient on soil constituents (Grčman et al., 2001). Synthetic chelates appear to mobilize micronutrients from the exchangeable, organic, and carbonate-bound fractions, but not from the oxide fraction (Elliott and Shastri, 1999). The use of chelating agents may induce the solubilization of other than the target micronutrients, which may become phytotoxic (e.g., Al and Mn).

11.5.6.2.2 Phosphate Compounds

Phosphate compounds can enhance the immobilization of micronutrients in soils by various processes including direct adsorption by P compounds, phosphate anion-induced adsorption, and precipitation with solution P as phosphates (Bolan et al., 2003b). Because the phosphate anion is very effective in desorbing certain oxyanions, such as selenite and molybdate, it is often used as an extractant to measure the amount of adsorbed oxyanions (James et al., 1995; Aide and Cummings, 1997). Phosphate also competes strongly with molybdate (MoO_4^{2-}) for adsorption sites, thereby resulting in increased desorption of the latter (Barrow, 1973; Xie et al., 1993).

Interaction of P with micronutrients also occurs within the plant. For example, increasing levels of P can induce or accentuate symptoms of Zn deficiency in plants grown in soils or culture media low in available Zn (Loneragan et al., 1979; Cakmak and Marschner, 1987). This disorder is commonly known as "P-induced Zn deficiency," which is the most widely examined P-trace element interaction in soil–plant systems (Loneragan and Webb, 1993). Five plausible mechanisms involving P, which may operate separately or concurrently, can cause decreases in Zn concentrations in the plant, depending upon plant species and environmental conditions (Loneragan et al., 1979; Loneragan and Webb, 1993): (1) dilution of tissue Zn by growth promoted by P addition, (2) inhibition of Zn uptake by roots as a result of competition with the cations accompanying the P, (3) increased P-induced Zn adsorption by Fe and Al oxide-rich variable charge soils, (4) greater Zn requirement in shoots induced by P additions, and (5) inactivation of Zn within the shoot in the presence of high P levels (Loneragan and Webb, 1993).

11.5.6.2.3 Liming Materials

Although liming is primarily aimed at ameliorating soil acidity, bioavailability of Zn, Mn, Cu, and other cationic micronutrients can be reduced as a result of decreased mobility by increased sorption/precipitation and competition between Ca^{2+} and micronutrients ions on the root surface for uptake (Brown et al., 2009). Because liming also increases Mo (molybdate) mobility in soils by decreased sorption on soil surfaces, Mo in soil solution available for uptake is increased.

11.5.6.2.4 Organic Composts

The most important organic fertilizers are biosolids and animal manures. Unlike biosolid application, regulations governing livestock and poultry manure are generally based on total N and P loading so that excessive amounts of some micronutrients are inadvertently applied (Cu and Zn in swine and As in poultry manure) (Bolan et al., 2004), requiring pretreatment to reduce bioavailability. For example, treatment of poultry manure with alum [$Al_2(SO_4)_3$] decreases the concentrations of water-soluble Zn and Cu. Organic amendments increase the CEC of soils, thereby resulting in increased micronutrients adsorption.

Micronutrients form both soluble and insoluble complexes with organic materials, a process that depends on the nature of the organic matter (Bolan et al., 2003a). With increasing pH, carboxyl, phenolic, alcoholic, and carbonyl functional groups on SOM dissociate, thereby increasing the affinity of ligand ions for micronutrient cations. For example, addition of manure increases the adsorption and complexation of Cu by the soil with DOC being primarily responsible (Bolan et al., 2003a).

11.5.7 Bioavailability Implications for Soil Testing and Risk Assessment

11.5.7.1 Soil Testing and Crop Response

While most soil testing focuses on the bioavailable fraction of micronutrients for fertilizer recommendation purposes, most risk assessment models assume that the target element is 100% available, which is clearly not the case; consequently, a number of soil tests have been developed to predict micronutrient availability. Descriptions of micronutrient deficiency symptoms and the soil conditions in which deficiencies are likely to occur are presented in Table 11.18 while selected references on crop responses to micronutrients are presented in Table 11.19. In this section, we focus on Zn, Mn, Cu, Fe, B, Cl, Mo, and Ni that are essential for crop growth, development, and yield.

TABLE 11.18 Deficiency Symptoms and Crop Response to Micronutrients

Micronutrient	Deficiency Symptoms	Crop Response
Boron	B deficiencies symptoms vary with plant species including impaired meristem activity (dieback of young growth, malformed leaves often manifest as "witches broom"), impaired cell wall development (cracking of stem and petioles), and poor pollen tube development (reduced seed set, fruit fall, and deformed fruit)	B deficiency occurs on a wide range of soils (coarse-textured, highly weathered, shallow, volcanic ash, and thin soils over calcareous material) and crops
Cobalt	Co is essential for N fixation in plants Deficiency causes ill-health in ruminants. Co deficiency is associated with vitamin B12 decreases in animals	Co deficiency occurs in acidic and highly leached soils, soils derived from granites, calcareous, and peat soils Co is usually administered directly to animals
Copper	Catalyst for several enzymes Deficiency effects new growth with wilting, withering of youngest growth Cu deficiency in grain crops is known as reclamation disease, wither-tip, yellow-tip, or blind ear. In woody plants, such as citrus, this is known as dieback or exanthema	Cu deficiency occurs in: peat and muck soil; alkaline and calcareous soils, especially sandy soils or those with high levels of free $CaCO_3$: highly leached soils; or soils heavily fertilized with N, P, and Zn fertilizers Cu deficiency is corrected mostly by soil application rather than foliar application; Cu is also applied as a fungicide spray
Iron	A major element for chlorophyll production. Deficiency turns new leaves pale yellow or white while the veins remain green Difficult for plants to absorb and moves slowly within the plant. High soil pH prevents plants absorption of Fe	Fe deficiency is caused by imbalance of metallic ions (Cu and Mn), excessive P, a combination of high soil pH, high lime application, high soil moisture, cool temperature, and high levels of bicarbonate in the rooting medium Fe deficiency can be corrected by direct application of Fe fertilizer to soils or as foliar application
Manganese	Works with plant enzymes to reduce nitrates before producing proteins Mn deficiency turns young leaves a mottled yellow or brown Mn deficiency is called gray speck in oats, yellow disease in spinach, speckled yellow in sugar beets, marsh spot in peas, crinkle leaf in cotton, stem streak necrosis in potato, streak disease in sugarcane, mouse ear in pecan, and internal bark necrosis in apple	Mn deficiency occurs in: shallow peaty soils overlying calcareous subsoils; alluvial soils and marsh soils derived from calcareous parent materials; poorly drained calcareous soils with high organic matter; acid sandy mineral soils that are low in native Mn or high lime application Mn deficiency is corrected by soil application of Mn fertilizers or by foliar application
Molybdenum	Mo is an essential constituent of enzyme necessary for N_2 fixation. Deficiency causes leaves to turn pale, with scorched-looking edges, and irregular growth. Mo deficiency is known as whiptail disease in brassica plants and yellow spot disease in citrus. Mo deficiency is frequently associated with legume crops as Mo is an essential constituent of N_2 fixation	Mo deficiency occurs in acid sandy soils, highly podsolized soils, highly weathered tropical soils and well drained sandy soils Mo deficiency can be corrected by soil application, foliar spray, and seed treatment with Mo; lime application can overcome Mo deficiency
Nickel	A constituent of four enzymes: urease, methyl coenzyme M reductase, hydrogenase, and carbon monoxide dehydrogenase Without Ni, toxic levels of urea accumulate, leading to the formation of necrotic lesions. In tomato, chlorosis in the youngest leaf leading to necrosis of their meristematic tissues; in cereals (wheat, oats, and barley) growth depression, premature senescence and decreased Fe levels	Occurs mainly in woody perennials such as pecan and coffee. Can be induced as a result of complexation by glyphosate. Foliar sprays are effective in overcoming deficiency
Selenium	Essential for higher animals; Se deficiency causes muscular dystrophy or white muscle disease	Se deficiency occurs in strongly leached soils
Zinc	Zinc is required in a number of enzymes and plays an essential role in DNA transcription Deficiency produces stunting, yellowing, and curling of small leaves A typical symptom of deficiency is the stunted growth of leaves, commonly called "little leaf" and is caused by the oxidative degradation of the growth hormone auxin	Zn deficiency is caused by: low Zn content in soils, high lime application, or unavailability of Zn to the plant, and metabolic disorder within plants (e.g., imbalance between Zn and P) Zn deficiency can be overcome by soil and foliar application and avoiding imbalance between Zn and P

Source: Adriano, D.C., *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risks of Metal(loid)s*, 2nd edn., Springer, New York, 2001.

11.5.7.1.1 Diagnosis and Prognosis of Micronutrient Deficiencies or Toxicities

Dry matter and grain yield of a crop are determined by the ability of the roots of plants to extract micronutrients from the soil at rates that are nonlimiting for crop growth. Therefore, the amount of nutrient taken up by a crop is a measure of availability. Analysis of selected plant parts (e.g., leaves, young growth), or whole shoots (Smith, 1980), is used as a diagnostic tool to identify micronutrients that may be limiting growth in contrast to soil tests that estimate the available pool. Plant analysis as a diagnostic tool is discussed in detail in Chapter 13.

TABLE 11.19 Selected References for Crop Responses to Micronutrients

Micronutrient	Crop Species	Application Rate	Observations	Reference
Cu	Barley (*Hordeum vulgare* L.) and wheat (*Triticum aestivum* L.)	50 kg Cu ha^{-1}	Application levels about 4–5 times the usual for crop application. However, no detrimental effects in yield reduction or phytotoxicity in wheat. For barley, 50 kg Cu ha^{-1} decreased yield by 12% in the first year. The Cu levels in plants were <9 mg kg^{-1}	Gupta and Kalra (2006)
	Wheat	6.7–13.4 kg Cu ha^{-1}	Application of Cu increased grain yield	Rehm (2008)
	Wheat and barley	0.7–2.1 kg Cu ha^{-1}	Application of Cu increased grain yield and concentrations of wheat and barley grown on neutral to acidic soils	Gartrell and Glencross (1968)
Zn	Barley and wheat	50 kg Zn ha^{-1}	Zn applications of 50 kg ha^{-1} for 2 years resulted in crop tissue Zn levels as high as 105 mg kg^{-1} did not cause any phytotoxicity in cereals	Gupta and Kalra (2006)
	Rice	13.5 kg Zn ha^{-1}	Zn at 13.5 kg ha^{-1}, increased dry matter, tissue Zn concentration and grain yield	Slaton et al. (2005)
	Wheat and barley	0.7–2.1 kg Zn ha^{-1}	Application of Zn increased grain yield of wheat and barley grown on neutral to acidic soils	Gartrell and Glencross (1968)
Fe	Soybean and Pigeon pea	20 kg Fe ha^{-1}	Application of Fe at 20 kg Fe ha^{-1} increased grain yield of soybean and pigeon pea by 9% and 414%, respectively	Hodgson et al. (1992)
	Soybean	400 g Fe EDTA (5.5% Fe and 2% EDTA) ha^{-1}	The Fe application with 80 kg N ha^{-1} gave the highest seed yield	Caliskan et al. (2008)
Co	Faba bean (*Vicia faba* L.)	20 mg L^{-1} Co as foliar spray	Co application at 20 mg L^{-1} increased grain yield by 218% and total protein by 48%	Hala (2007)
Mn	*Lupinus angustifolius* L.	1.7 kg Mn ha^{-1} in 200 L foliar application	Foliar Mn prevented deficiency, and increased grain yield	Hannam et al. (1984)
	L. angustifolius L.	3.5–15 kg Mn ha^{-1}	Soil application increased grain yield, decrease amount of split seed at maturity	Brennan (1999)
Ni	Tomato	30 mg Ni kg^{-1} soil	This level, increased quality of fruit and auxin and gibberlin contents	Gad et al. (2007)
	Pecan (*Carya illinoinensis* [Wangenh.] K. Koch)	10–100 mg L^{-1} (plus urea and surfactant)	Decreased "water-stage fruit-split" symptom of pecan reducing crop losses	Wells and Wood (2008); Malavolta and Moraes (2007)
Mo	Tobacco	1.1 kg Mo ha^{-1}	This level of Mo and lime at 7.3 or 14.6 t ha^{-1} increased yield by 16%–22%	Khan et al. (1994)
Se	Wheat	20 g Se ha^{-1}	Se fertilization at 20 g ha^{-1} increased grain Se content by four- to sevenfold	Stroud et al. (2010)

11.5.7.1.2 Soil Analysis to Assess Available Micronutrient Pool

The objectives of a micronutrient soil test are to (1) group soils into classes for fertilizer recommendations, (2) predict the probability of a response to an application, and (3) evaluate soil productivity (Fitts and Nelson, 1956). A good soil test should (1) extract all or a proportionate fraction of the available form or forms of a nutrient, (2) accurately and in a timely manner measure the amount of the nutrient extracted, and (3) be correlated with the growth and response of each crop to each micronutrient under various conditions (Sims and Johnson, 1991). A detailed discussion of soil testing is presented in Chapter 13.

11.5.7.1.2.1 Zinc Zinc deficiency is widespread throughout the world, probably the most common micronutrient deficiency across a range of crop species (Takkar and Walker, 1993). Usually, Zn deficiency in plants occurs in calcareous (high pH) soils because of low Zn availability or in coarse-textured (sandy), highly leached, acid soils because of their low total Zn content. Antagonisms between Zn and several other essential elements (e.g., P, N, and Cu) can also lead to Zn deficiencies (Loneragan and Webb, 1993). Recommended amounts of Zn fertilizer range from about 1 to 15 kg Zn ha^{-1}. Some crops particularly sensitive to inadequate soil Zn are corn, soybean, rice (*Oryza sativa*), field bean (*Vicia faba*), and citrus (*Citrus spp.*).

The sources of Zn used as fertilizers are presented in Table 11.16 with zinc sulfate crystal or granular form being the most common (Mortvedt and Gilkes, 1993). Zinc oxide has low effectiveness in the granular form as it is insoluble in water (Mortvedt, 1991). Because water solubility of the Zn source is important, at least 50% water solubility is required to be effective on calcareous soils (Gangloff et al., 2002; Westfall et al., 2002). However,

in acid soils, a wide range of products, including the oxide and sulfate, are equally effective as fine powders mixed thoroughly with the soil (Mortvedt and Gilkes, 1993).

11.5.7.1.2.2 Copper Usually, Cu deficiency occurs on highly leached, acid soils (low total Cu content), on coarse-textured (sandy) soils, and soils rich in organic matter. Recommended amounts of Cu fertilizer range from about 1 to 25 kg Cu ha^{-1}. Because amounts of Cu in excess of crop requirements are often applied particularly in manures and fungicides, Cu has a long residual effect in the soil and remains bioavailable for some considerable time after application; consequently, frequent applications are not required (Gartrell, 1981; Brennan, 2006).

Although soil applications are the commonest method used to correct Cu deficiency (Gartrell, 1981; Martens and Westermann, 1991), foliar sprays are effective in citrus, wheat, corn, and soybean (Martens and Westermann, 1991). Because some fungicides usually supply more Cu than is required by the crop, repeated applications can result in soil accumulation (Graham and Webb, 1991). Inorganic sources applied to the soil such as, Cu oxide, sulfate, carbonate, nitrate, and chloride are effective in correcting deficiencies in crops (Gartrell, 1981).

Bioavailability of Cu fertilizers is affected by (1) the method of placement, (2) ability of the Cu product to produce Cu^{+2} ions in the soil or rhizosphere, (3) reactions of Cu with soil, and (4) different requirements of plant species due to differences in growth rate, efficiency of absorption, or translocation in the plant. Because Cu is immobile in the soil, its availability is greatly influenced by the number of granules per unit volume of soil and the position in which they are placed. Banding Cu is more effective than topdressing, without incorporation into the soil. Copper fertilizer is ineffective in soil profiles that contain few absorbing roots, for example, dry soil. Applied at the same rate, large granules (fewer granules per unit volume) are much less effective than fine material (Gartrell, 1981).

11.5.7.1.2.3 Manganese Usually, Mn deficiency is associated with well-drained neutral to alkaline soils, and those rich in organic matter. In addition, because of their low total Mn content, highly leached, coarse-textured (sandy) acid soils are also frequently deficient for some crop species. Recommended amounts of Mn fertilizer range from about 2 to 20 kg Mn ha^{-1}. Manganese has a short residual effect in most neutral to alkaline soils, because the bioavailable Mn^{+2} is rapidly oxidized to MnO_2. On the other hand, for sweet lupin (*Lupinus angustifolius* L) grown on acid sandy soils, the effect of 7.5 kg Mn ha^{-1} has lasted for some considerable time after application, while that of 50 kg Mn ha^{-1} persisted for about 17 years (Brennan et al., 2001). Foliar application is the most efficient and effective method of correcting Mn deficiency in various crops grown on a range of deficient soils. Manganese deficiency is frequently encountered in cereals, cotton, peanuts, soybeans, and a range of fruits and vegetables (Martens and Westermann, 1991).

Band placement of manganese sulfate fertilizer is more effective than broadcasting at the same rate for soybean (*Glycine max*) (Mascagni and Cox, 1985) and sweet lupin (Brennan, 1999) because concentration in the band reduces the rate of oxidation of Mn^{+2} to less available forms. Foliar sprays and band application of Mn sulfate were equally effective for soybeans (Mascagni and Cox, 1985). Soil moisture affects Mn availability with the seed-applied Mn being effective under adequate soil moisture but not drought conditions in soybean (Alley et al., 1978). For some crops (peanut [*Arachis hypogaea*], soybean, and wheat) and conditions, multiple rather than single foliar sprays are required (Cox, 1968; Hallock, 1979; Nayyar et al., 1985). The timing of the foliar spray in relation to crop development stage is also important for soybean (Gettier et al., 1984), corn (Mascagni and Cox, 1984), and sweet lupin (Brennan et al., 2008).

11.5.7.1.2.4 Iron Usually, Fe deficiency is a common problem in numerous crop species grown on alkaline soils containing free $CaCO_3$ in the soil profile (Marschner, 1995). In many cases, the problem stems from various factors that inhibit Fe absorption by plant roots or impair its utilization in metabolic process in Fe-inefficient species. Although rare, acid soils with deficient levels of Fe do occur, for example, in Florida and other similar areas (Welch et al., 1991). Recommended amounts of Fe fertilizer range from about 20 to 100 kg Fe ha^{-1} (Martens and Westermann, 1991). Iron has a short residual effect in most alkaline soils, because Fe^{+2} is rapidly converted to unavailable forms. Foliar application is more effective at correcting Fe deficiency in various crops grown on a range of deficient soils. Iron deficiency is frequently encountered in a range of Fe-sensitive crops and/or Fe-inefficient cultivars (Welch et al., 1991). Growing Fe-tolerant species or varieties is an effective method for controlling Fe deficiency in crops grown on soils where Fe availability is low (Chen and Barak, 1982).

Because soil–fertilizer contact is limited in band placement, iron sulfate fertilizer banded in the soil is more effective than broadcasting at equal rates. However, Fe sulfate is frequently broadcast on pastures (*Trifolium subterannean* L.) where Fe deficiency has been induced by overliming acid soil (Brennan and Highman, 2001). Several other methods such as (1) mixing of Fe sulfate and sulfuric acid (Wallace, 1988; Martens and Westermann, 1991), (2) inclusion of organic residues with Fe sulfate (Mostaghimi and Matocha, 1988), and (3) inclusion of K_2SO_4 with Fe sulfate that corrected Fe deficiency in peanuts (Shaviv and Hagin, 1987) have been used to reduce the conversion of applied Fe to unavailable forms. Foliar sprays of inorganic (e.g., Fe sulfate) and organic Fe sources (e.g., Fe chelates) are very effective in correcting Fe deficiency (Martens and Westermann, 1991). Foliar applications of Fe sulfate are more effective than soil application of Fe chelate (FeEDDHA). Iron is less available in well-aerated soils due to insolubility of Fe(III) oxides; but availability can be promoted by increasing soil moisture that produces loci where some reduction of Fe(III) to Fe^{2+} can take place (Bjerre and Schierup, 1985). However, excessive soil moisture in calcareous soils may intensify Fe deficiency mainly due to the buildup of HCO_3 in the soil solution (Moraghan and Mascagni, 1991). Plant residues, manures, biosolids, charcoal, coal, and a range of by-products from manufacturing (e.g., polyflavoids and

lignosulfonates) have been effective in alleviating Fe deficiency (Chen and Barak, 1982).

11.5.7.1.2.5 Boron Boron is an essential micronutrient where the range between deficiency and toxicity is smaller than for most other micronutrients. Plants respond to the activity of B in solution rather than to adsorbed B making the rate of desorption, which follows a first-order rate equation, important in B supply to the root. The bioavailability of B is determined by pH, texture, moisture, temperature, SOM, and clay mineralogy (Goldberg, 1997) while the adsorbing surfaces of importance are sesquioxides, clay minerals, lime, and organic matter. Boron adsorption increases initially with pH on both mineral and organic surfaces up to pH 8–10 and then decreases. Consequently, overliming acid soils can cause a temporary deficiency due to higher adsorption at high pH (Reisenauer et al., 1973). The roles of B in the plant include sugar transport, cell wall synthesis and structure, pollen tube growth, pollen viability, carbohydrate synthesis, respiration, and membrane integrity while excess B can cause impairment in a range of cellular functions, such as phenol and ascorbate metabolism, free radical generation, and detoxification (Cakmak and Romheld, 1997); but its primary role is still unknown. These changes may be direct or indirect functions of B deficiency.

Boron deficiency occurs on a wide range of soils (coarse-textured, highly weathered, shallow, volcanic ash, and shallow soils over calcareous material) and crops (alfalfa [*Medicago sativa*], beets [*Beta vulgaris*], peanut [*A. hypogaea*], brassicas [*Brassica* spp.], coffee [*Coffea* spp.], oil palm [*Elaeis guineensis*], cotton [*Gossypium* spp.], sunflower [*Helianthus annuus*], apple [*Malus domestica*], and grape [*Vitis vinifera*]) (Shorrocks, 1997) as well as many vegetable crops.

Deficiency symptoms vary with plant species including impaired meristem activity (dieback of young growth, malformed leaves often manifest as "witches broom"), impaired cell wall development (cracking of stem and petioles), and poor pollen tube development (reduced seed set, fruit fall, and deformed fruit). The main B sources used to correct B deficiency are borax ($NaB_4O_7 \cdot 10H_2O$ [11% B], NaB_4O_7 [21.4% B]), boric acid ($B(OH)_3$ [17.5% B]), and a range of crushed ores containing variable amount of B (Shorrocks, 1997). Boric acid and Solubor® (17.5% B), products readily soluble in cold water, are used as foliar applications. For annual crops, 1–2 kg B ha^{-1} is the recommended rate (Shorrocks, 1997).

Boron toxicity commonly occurs in arid and semiarid environments on alkaline and saline soils (Nable et al., 1997). Continued application of irrigation water with high levels of B can lead to toxicity. The typical symptoms of B toxicity are leaf burn, chlorotic, and necrotic patches often on the margins and tips of older leaves (Bennett, 1993).

11.5.7.1.2.6 Chloride Chloride (Cl^-) is essential for many plant functions such as a chemical balancing agent for K^+ during the opening and closing of stomata, photosynthesis, cation balance and transport within the plant, counteracting the effects of fungal infection, and competing with NO_3^-, thus promoting the uptake of NH_4-N (Boyer et al., 1954; Fixen, 1993; Talbott and Zeiger, 1996). Deficiency symptoms vary with plant species including wilting and leaf chlorosis while toxicity manifests itself as leaf margin scorching, leaf drop in excessive situations, and leaf area reduction and thickening, resulting in reduced growth.

Because Cl^- is highly soluble in water, leaching losses occur, where rainfall is high and soil drainage is good. If Cl^--containing fertilizers (e.g., muriate of potash [KCl]) are not regularly used, Cl^- deficiency can occur. In coastal regions with rough surf, atmospheric deposition of Cl^- can be high, decreasing with distance from the coast. Chloride competes with other anions (e.g., NO_3^-, SO_4^{2-}) although little data are available on the specific interactions and competition between each anion.

11.5.7.1.2.7 Nickel Recently Ni, which has been shown to be an essential element for plants, is required in miniscule amounts as a piconutrient. It plays a vital part in the translocation of N in ureide-transporting woody perennials such as pecans (*Carya illinoensis*) and coffee (*Coffea arabica*) where a deficiency of Ni disrupts ureide, amino, and organic acid metabolism but its physiological role is poorly understood (Bai et al., 2006). In addition, it confers disease resistant on plants although much work needs to be done in this field (Wood and Reilly, 2007). Nickel appears to play a key role in the production of secondary plant metabolites that influence resistance to disease. Most soils contain adequate amounts of Ni but under certain specific conditions, for example, where glyphosate that strongly complexes Ni has been used as a herbicide, deficiencies can be induced (Yamada, 2010). Consequently, deficiency symptoms manifest themselves as those of N. Research in this field is still in its infancy.

11.5.7.1.2.8 Molybdenum Because Mo occurs in the soil solution as MoO_4^{2-}, it interacts with other anions, particularly phosphate and SO_4^{2-} to reduce Mo uptake. In addition, it is strongly sorbed on sesquioxide surfaces at pH values below 7, decreasing 100-fold for each unit drop in pH. Thus, Mo deficiencies are mainly found on acid soils where bioavailability is low (Gupta, 1997). Consequently, liming acid soils can often supply sufficient Mo to meet the needs of many crops including legumes, which are most sensitive to deficiency. In legumes, because Mo is required by the Rhizobia in the fixation of N, deficiency of Mo is manifest as those of N. In addition, it is an activator for the nitrate reductase enzyme, crucial to the N nutrition of crops. Where Mo deficiency occurs, correction can be achieved by relatively small applications (~100 g Mo ha^{-1}) as foliar sprays in the form of sodium or ammonium molybdate.

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